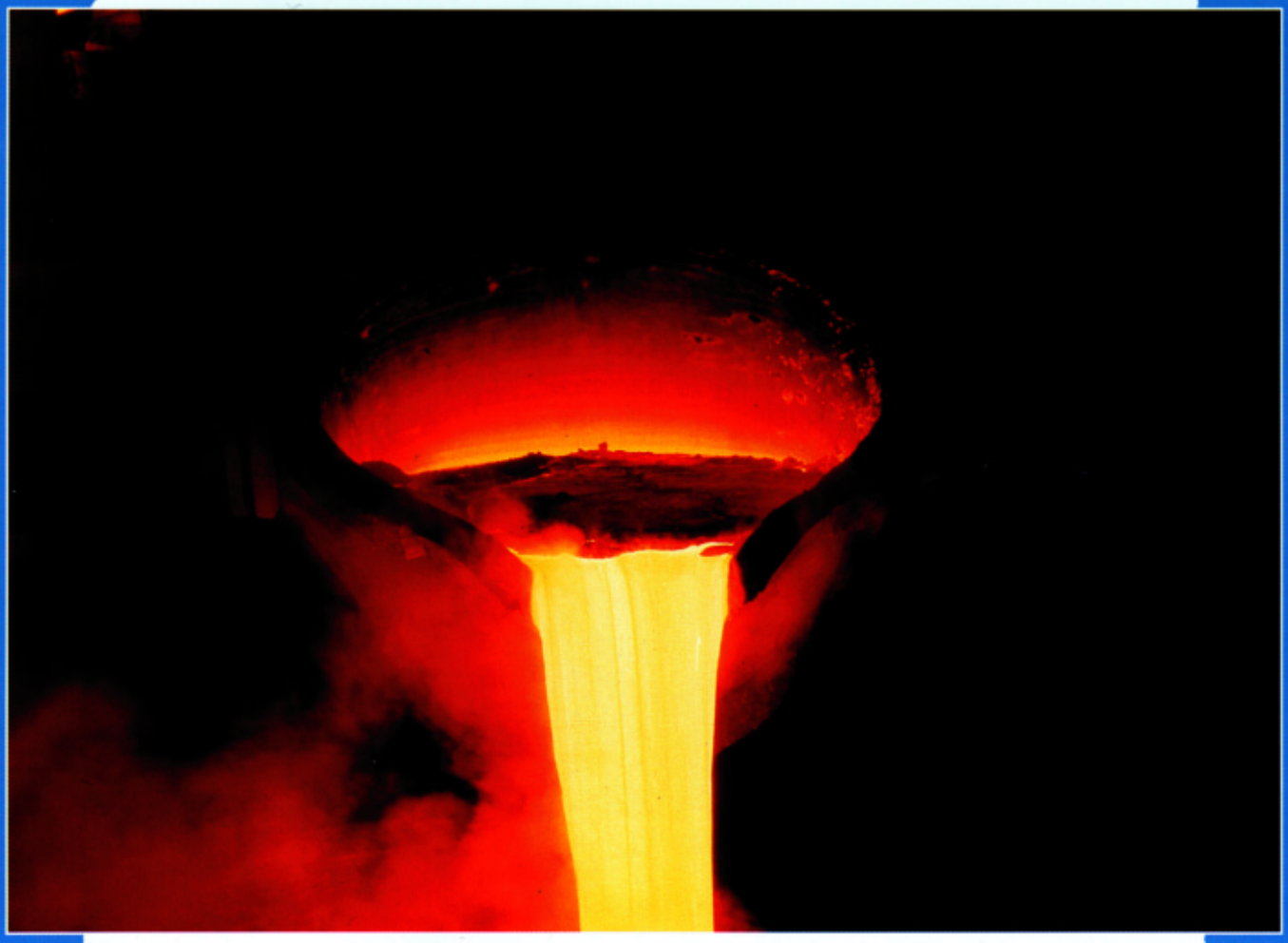
ENVIRONMENTAL PROTECTION

Marja Riekkola-Vanhanen

Finnish expert report on best available techniques in copper production and by-production of precious metals



FINNISH ENVIRONMENT INSTITUTE

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Foreword

The European Council Directive on Integrated Pollution Prevention and Control (IPPC-Directive, 96/61/EC of September 24, 1996) is aimed at an integrated approach of prevention and control of pollution arising from categories of industrial activity listed in its Annex I. According to article 16.2 of the Directive the Commission shall organise an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring, and developments in them. This information should lead to a European Best Available Techniques reference document (BREF) on each industrial sector.

One of the activities included in the Directive concerns the production of non-ferrous metals, according to the definition of category 2.5 (a) in Annex I: ”Installations for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes”. These installations are part of the industrial sectors to be studied in 1998.

Within the above mentioned framework, the Finnish Environment Institute and Outokumpu Technology Oy have decided to contribute to the exchange of information in the European Union by making a study on Best Available Techniques for the primary production of non-ferrous metals. Outokumpu Research Oy has been requested to perform this study. Raimo Rantanen is responsible for the work and the report has been written by Marja Riekkola-Vanhanen. Maija-Leena Metsärinta has prepared a literature survey on the subject.

Primary non-ferrous metal production in Finland concerns only copper, nickel, zinc and ferrochromium. Gold and other precious metals are produced as by-products of copper production. This report describes the primary production of copper and the production of gold and other precious metals as by-products. The primary production of nickel, zinc and ferrochromium are described in separate reports.

The main objective of this BAT report is to identify available techniques for the reduction of emissions and energy use in the primary copper production in Finland. Only the pyrometallurgical flash smelting process is in use in Finland to recover copper from sulphide concentrates and is the main process described in this report. The information presented is largely based on environmental permit applications, the corporate environmental programme and permit regulations concerning Outokumpu. Additional information concerning general issues of copper production and comparisons is obtained from the available literature.

The project has been guided by a steering group that provided comments on the draft reports and offered a platform for discussion on the scope, themes and results of the study. The steering group members represented the following organisations: Finnish Environment Institute, Southwest Finland Regional Environment Centre, Outokumpu Oyj, Outokumpu Technology Oy, Outokumpu Harjavalta Metals Oy, Outokumpu Zinc Oy and Outokumpu Chrome Oy.

Contents

1 General Information

Metallic copper has been found at several locations in the world. It was known to early man in about 7000 BC. Its early uses were in jewellery, utensils, tools and weapons. Its use increased gradually over the years and then saw a dramatic growth in the 19th and 20th century with the mass adoption of electricity. Copper is an excellent conductor of electricity and heat and is easily worked into wire, rod and cable. Electrical conductivity, corrosion resistance and thermal conductivity are still the properties most exploited in the use of copper /1/.

Copper is most commonly present in the Earth's crust as copper-iron-sulphide and copper sulphide minerals such as for example chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S). The concentration of these minerals in an orebody is low. Typical copper ores contain from 0.5 to 2 % copper. Pure copper metal is mostly produced from these ores by concentration, smelting and refining.

Copper also occurs in oxidised materials, carbonates, oxides, hydroxy-silicates and sulphates, but to a lesser extent. Copper metal is usually produced from these minerals by hydrometallurgical methods. Hydrometallurgy is also used to produce copper metal from secondary sulphide minerals, e.g. chalcocite (Cu_2S) and mine waste dumps.

A third major source of copper is recycled copper. Secondary raw materials account for about 40 % of the use of copper and its alloys in Europe and worldwide.

The core of the EU copper industry is in smelting, refining and semi-manufacturing, as the mining capacities are negligible. There is sizeable copper mine production only in Portugal (Neves Corvo, 106,500 tons of copper in 1997) and Sweden (Boliden, 86,600 tons of copper in 1997). According to these figures, the EU accounts for around 2 % of the world copper mine output (Table 1).

Table 1. Copper production 1997 in 1000 tons of copper /2/.

Area	Mine	Smelter	Refinery
EU	239	1 168	1 854
NonEU Europe	1 135	1 310	1 271
Africa	642	562	531
Asia	1 884	3 330	3 630
America	6 952	4 586	6 000
Oceania	672	208	271

Annual refined copper production in the EU reached 1,854,000 tonnes in 1997 which is 13.7 % of worldwide production. Refinery output is in the form of cathodes that are often melted and cast on the premises into billets, cakes etc. About 60 % of the feed supplies to the EU copper smelters and refineries are purchased on the international market in the form of copper concentrates, blister copper or scrap. The remaining 40 % come from domestic copper concentrates as well as domestic copper scrap. EU copper production is presented in Table 2.

EU copper demand follows the slow growth pattern of a mature market. Recycling is at a high level as copper can be reprocessed without the loss of its

intrinsic properties and many secondary materials are available. Refining capacity in the EU countries has been able to grow primarily by securing raw materials on the international market and making use of copper or brass scrap and residues generated by consumers and processors. Computer scrap and printed circuit boards are becoming more common secondary sources.

Table 2. European copper production 1997 in 1000 tons of copper /61/.

	Mining	Refining
Benelux		203
Finland	9	116
France		6
Germany		296
Italy		6
Portugal	108	
Spain	37	229
Sweden	87	95
UK		9
Total EU	239	959
Norway	7	33
Poland	417	421
Macedonia	87	104

There are five major refineries in the EU which use mainly primary raw materials. These producers are presented in Table 3. It is estimated that the copper refining industry employed more than 5000 people in 1994.

Table 3. Primary refined copper producers in EU.

Country	Company	Location	Capacity t/y
Spain	Atlantic Copper S.A.	Huelva	250 000
Sweden	Boliden Mineral AB	Rönnskär	128 500
Germany	Norddeutsche Affinerie AG	Hamburg	380 000
Finland	Outokumpu Harjavalta Metals Oy	Harjavalta, Pori	125 000
Belgium	Union Miniere	Hoboken, Olen	285 500

The potential for expansion of copper smelting capacities in the EU is limited due to the access to feed supplies and the heavy investment costs. However, nearly all of the primary smelters have increased production output. This significant increase in production capacity has been made simultaneously with environmental improvements.

The demand for copper comes mainly from the electrical and electronics industries, about 50 % of total EU consumption. The construction sector, plumbing, roofing, decoration etc. accounts for 25 % of consumption. The rest is used in industrial machinery and equipment, transportation equipment and consumer products. Copper applications are well developed and the growth pattern of copper consumption closely follows the cycle of industrial activity in general.

The price of metallic copper is generally governed by the London Metal Exchange (LME) quotations for Grade A copper. Price trends reflect the global balance of supply and demand, but are of course susceptible to speculative influences and imbalances in the global distribution of the metal. In addition to providing the industry with a price reference, the LME offers a hedging medium against price fluctuations.

Recycling is at a high level as copper can be reprocessed without loss of its intrinsic properties and many secondary materials are available. The EU copper refining industry has been able to grow primarily by securing raw materials on the international market and making use of scraps and residues generated by consumers and processors. At the same time it has been able to comply with increasingly stringent environmental constraints.

2 Applied Processes and Techniques

Approximately 90 % of the world copper production from ores is now manufactured from sulphidic ores by pyrometallurgical techniques (see Figure 1). Five steps can be distinguished in the primary production of copper:

I. mining of copper ores
II. isolation of the copper mineral particles in an ore by flotation
III. smelting of the resulting concentrate to molten high copper matte
IV. converting of molten matte to molten blister copper
V. fire- and electrorefining of the blister to pure copper.

This study focuses on the smelting, converting and electrorefining steps. The mining and flotation processes are also excluded in the EU Reference Document on Best Available Techniques in Non Ferrous Metals Industries. Table 4 shows world copper smelter capacities and production in 1995 /61/.

Hydrometallurgical production of copper from ores has become more important in the past decade. The materials most commonly treated this way are oxide and secondary sulphide copper minerals. Today more than 10 % of the world mine production of copper is produced by hydrometallurgical processes and the growth in this area is still continuing. It is expected that in the year 2000 more than 20 % of copper will be produced by leaching of copper ores or concentrates (see Figure 1).

Table 4. World copper smelter capacities and production in 1995.

Primary Copper Smelting Technology	Capacity Mt	Production Mt	Number of Smelters using this Technology	Number of Smelters using only this Technology
Outokumpu Flash Smelting	4.1	3.5	26	25
Reverbatory Furnace	2.8	1.8	27	16
Modified El Teniente Converter Converter	0.9	0.8	7	0
Electric Furnace	0.7	0.5	5	5
Blast Furnace	0.6	0.4	8	7
INCO Flash Smelting	0.5	0.4	3	2
Mitsubishi	0.4	0.3	2	2
Vanyukov	0.4	0.3	2	0
Isasmelt	0.3	0.2	2	1
Noranda Reactor	0.3	0.2	2	1
Contop	0.1	0.1	1	1
Baiyin	0.1	0.1	1	1
Total	11.1	8.6	76	61

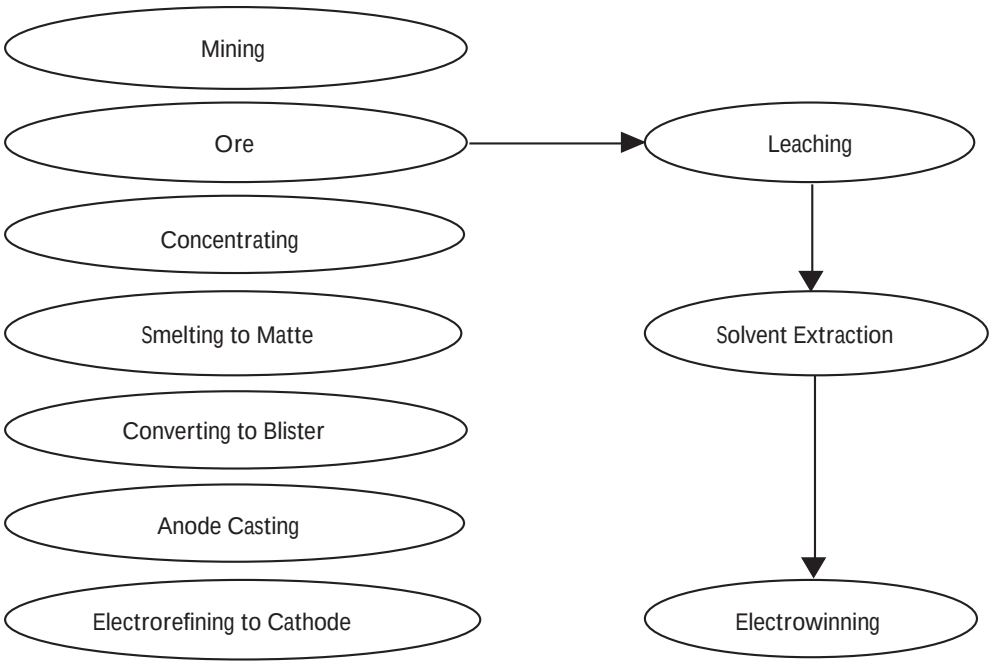

Figure 1. Flowsheet of primary copper production.

Only the pyrometallurgical copper process is used in Finland to recover copper from copper concentrates. This Flash Smelting process at Outokumpu Harjavalta Metals Oy is described in this study. A brief description is also given of the other copper producing processes applied elsewhere. The processes developed by Outokumpu and used also outside the EU are also described.

2.1 Pyrometallurgical Copper Production

2.1.1 Smelting of concentrate to matte

Matte smelting entails melting concentrate in a large furnace at about 1,200°C in an oxidising atmosphere. The objective of the smelting is to oxidise some of the sulphur and iron in the concentrate and to produce a molten sulphide phase (matte) rich in copper and to separate the rest as slag.

The products of the smelting are molten sulphide matte, 35 to 70 % Cu, containing most of the copper in the concentrate feed and a molten oxide phase (slag) as free of copper as possible. The molten matte is subsequently converted in a converting furnace to form impure copper metal. The slag is discarded, usually after a copper recovery step.

Sulphur dioxide bearing gas is also generated. SO_2 is harmful to the environment and must be removed before the off gas is released. This is almost always done by recovering the SO_2 as sulphuric acid or liquid SO_2.

An important objective of matte smelting is to produce a slag which contains as little copper as possible. This is done by keeping the slag near silica saturation and by keeping the furnace sufficiently hot that the slag is molten and fluid.

Smelting is most often performed in flash furnaces. It used to be carried out to a considerable extent in reverbatory furnaces, but this older technology is being replaced.

2.1.2 Flash furnace smelting

The oxidation reactions provide much or all of the energy for heating and melting of the products. Fossil fuel burners are often employed to control furnace temperatures, but mostly the process is autogeneous. The oxygen enrichment degree is used for the temperature control. The molten matte and slag are tapped separately from the furnace as they accumulate.

There are three types of industrial flash furnaces in use: the Outokumpu type, which uses oxygen enriched air as the oxidant (Figure 2); the Inco type, which uses technical oxygen as the oxidant; and the Contop application, which uses cyclone burners to introduce oxygen enriched air and concentrate into the smelting furnace. This application will be closed in Spring 1999.

Flash furnaces accounted for about 47 % of the world's copper concentrate smelting in 1995.

2.1.2.1 Reverbatory Furnace Smelting

Reverbatory furnace smelting accounted for most of the world's copper smelting as late as 1975. However, the last reverbatory smelter was built in 1976 and the existing furnaces are gradually being replaced by flash and other smelting furnaces.

The reverbatory furnace is a hearth furnace in which a solid charge of concentrates and flux is melted at about 1,200°C by hot combustion gases sweeping over the hearth. The combustion gases are provided by burning fossil fuel in endwall or roof burners. The products of the process are molten matte and molten slag.

Reverbatory furnace smelting is primarily a melting process in contrast to flash smelting which is an oxidation/melting process. Reverbatory smelting makes little use of the energy from sulphur and iron oxidation for heating and melting. It also produces large quantities of fossil fuel combustion gas containing about 1 % SO_2. It is difficult to remove SO_2 at this low concentration which means that the off-gases are an air pollution problem /1/.

2.1.2.2 Other smelting processes

In recent decades many new processes have been developed. These processes, like flash smelting, use the oxidation of iron and sulphur in the concentrate feed to provide energy for heating and melting.

The Isasmelt, Noranda, Teniente, Mitsubishi, Vanyukov and Baiyin processes use bath smelting. Oxygen enriched air is blown to the furnace with vertical lances or through submerged tuyeres. All these processes are discussed later in Chapter 4.

The Noranda process was commissioned at the company's Horne smelter in 1997. The process can produce blister copper when using concentrates with low impurity levels. The normal operating practice is to produce copper-rich matte to undergo further conversion.

The Teniente process is similar to the Noranda process. The main differences are the addition of "seed" matte, which is periodically added to the furnace to maintain the heat balance; the injection of dry concentrate through some of the tuyeres and the charging of moist concentrate above the bath; and the fact that no coal is included in the furnace charge. Six smelters use Teniente furnaces in conjunction with reverbatory furnaces /36,37/.

The Isasmelt process /39/ uses moist feed that is fed to the furnace continuously with fluxes. Fuel oil or coal and oxygen are injected into the furnace through a steel lance, which is submerged in the molten bath. The lance stirs the bath and produces a slag along with matte. The separation of the molten phases takes place

on a fore-hearth and they are tapped periodically. The furnace is normally used on a batch basis when conditions in the furnace, such as the gas blown through the lance, are changed at the end of the batch. Isasmelt is used in Cyprus and Mt Isa.

A few examples of traditional matte smelting processes also remain in use around the world, particularly electric furnace smelting and blast furnace smelting.

2.1.3 Converting

Copper converting consists of air oxidation of the molten matte from smelting. Converting removes the iron and sulphur from the matte to produce crude molten metallic blister copper (99 % Cu) which is sent forward to pyro- and electrorefining.

Liquid matte is transferred from the smelting furnace in large ladles and poured into the converter through a large central mouth. The oxidising blast is then turned on and the converter is rotated forcing the blast into the matte through a line of tuyeres along the length of the vessel. The heat generated in the converter by iron and sulphur oxidation is sufficient to make the process autogeneous.

Converting is done in two stages. The first is the slag forming stage, in which iron and sulphur are oxidised. The second stage is the copper-making stage, in which the sulphur in the CuS_2 is oxidised to SO_2.

Peirce-Smith converters account for 90 % of copper matte smelting. This is due to their simplicity and high chemical efficiency. There is, however, significant leakage of SO_2 into the atmosphere during charging and pouring. Several alternatives have therefore been developed. The Hoboken converter has an improved gas collection system. In the flash converter solidified and ground matte is smelted with oxygen enriched air in a closed flash smelting furnace.

2.1.4 Slag cleaning

The copper smelting furnace slag can be cleaned either in an electric furnace or in a slag concentration plant.

2.1.4.1 Electric furnace

Copper smelting furnace slag is tapped through slag tap holes along launders into the electric furnace. Coke and reverts are added through the furnace roof. Slag from the electric furnace is tapped into granulation or cast in blocks and sold or transported to the slag storage area. Matte from the electric furnace is periodically tapped through tapping holes and launders into ladles and transferred by cranes to converters for further treatment.

There are three or six electrodes in the electric furnace to supply energy into the furnace. Electric power is needed for the reduction reactions, heat losses and smelting of reverts. The reductive agent is coke. Electric furnace off-gases are first burned in an incinerator, then cooled and taken through a bag filter or a scrubber to the stack.

2.1.4.2 Slag concentrator

Molten slag is tapped through tapholes and along launders into ladles, where the slag is cooled controlled by water spraying. After cooling the ladles are transport-

ed and unloaded onto the slag stockpile, from which the slag is transported onto a grizzly where oversized lumps are broken. Metallic copper is separated as the grizzly oversize. The grizzly undersize is transported to the screening station where lumps, pebbles and fines are separated into separate bins. Grinding consists of autogenous lump mills and pebble mills. Both grinding stages are equipped with hydrocyclones. Flotation is carried out in three main stages. Recovered copper concentrate is thickened and filtered by a pressure filter. The filtered concentrate is conveyed into the dryer. Slag mill tailings are pumped into a nearby tailing area. The clarified water from the tailing pond is used as process water.

2.1.5 Copper refining, anode casting and electrorefining

Molten blister copper is refined in an anode furnace in order to remove the remaining sulphur and oxygen. The refined copper is cast in open anode-shaped moulds.

In electrorefining copper is first dissolved electrochemically from the impure anodes into the copper sulphate-sulphuric acid-water electrolyte and then deposited from the electrolyte onto copper or stainless steel cathodes.

Fully grown cathodes are removed from the cells, washed with water and packed. They are sold for melting, casting and fabrication of copper semi-products.

2.2 Single Furnace Coppermaking

Smelting and converting are controlled oxidation processes which produce SO_2, iron oxide and eventually copper. It seems natural that the two processes should be carried out in a single step, i.e. in one furnace.

Until now copper has been made in a single furnace at only two places, which use Outokumpu Flash Smelting. Copper concentrates containing over 35 % copper or special concentrates containing only small amounts of iron can be treated by the Direct Blister Flash Smelting Process. Suitable concentrates can be made from chalcocite or bornite-chalcocite ores which have high copper contents or whose copper/iron ratios are high compared to chalcopyritic concentrates.

2.3 Continuous Converting

Over the last decade there has been considerable pressure to modernise converter practice. Firstly, there is the need for even higher levels of sulphur recovery as environmental regulations are tightened around the world. Secondly, there is a drive to eliminate the batch operations inherent in conventional converter operations and thus both improve efficiency and sulphur capture of both the process and the fugitive gases. The scheduling of all the movements and activity which takes place in the converter aisle requires considerable skill if the operation is to be carried out efficiently.

The continuous flash converter was developed by Outokumpu and Kennecott and the first installation was built at Kennecott´s Garfield smelter in 1995.

The Mitsubishi process employs three interconnected furnaces, a bath smelting furnace, an electric slag cleaning furnace and a converting furnace /33/. The copper concentrate is smelted in the bath furnace to a copper matte and slag, then matte and slag overflow into the electric furnace where they are separated and a discardable slag is formed. The matte is then transferred by gravity flow into the converting furnace, where it is continuously converted into blister copper. The

converter slag is recirculated to the smelting furnace. Mitsubishi smelters were built in Naoshima and Kidd Creek in 1991 /32,34,35/.

2.4 Outokumpu Flash Smelting Process at Harjavalta Plant

The Flash Smelting Process involves several stages as described in Figure 2. These stages are briefly in this paragraph. The smelting and converting processes are situated in Harjavalta in Western Finland and the copper refinery in Pori, about 30 kilometres away. Outokumpu Harjavalta Metals Oy is part of the Base Metals business area of Outokumpu Oyj. In 1997 it produced 200,000 tons of copper and nickel in Harjavalta and Pori. Outokumpu Harjavalta Metals Oy produces nearly 30 products. A considerable amount of the production is exported.

The first copper smelter was built in Imatra in 1936. During the war it was rebuilt in Harjavalta in 1944. The Flash Smelting process was introduced in 1949. The copper electrolysis was built in 1941 in Pori next to the copper semi-products fabrication. In 1959 and 1960 the nickel Flash Smelting Furnace and nickel electrolysis began operation. The last expansion of the works was completed in 1996. The number of personnel is about 1,000. The number of personnel working only in the copper process is 540.

Nearly all parts of the works are certified to ISO 9002 requirements. The last departments will be certified in the near future. The EMAS system of the copper refining part in Pori was registered in 1998.

Safety functions are organised as an essential part of normal business unit operations.

2.4.1 Raw material reception and storage

Most of the raw materials are imported to Mäntyluoto harbour. The concentrate is unloaded directly to the harbour transit terminal from the ship with grabs. Railway wagons are loaded in the terminal with front-end loaders. The wagons are covered with hydraulic lids. The wagons are weighed electronically both in loaded and empty conditions. The loaded wagons are delivered by train to the Harjavalta works, which is located some 45 km from the harbour.

The concentrates are stored in Harjavalta in a large warehouse for 50,000 tons of concentrate.

2.4.2 Blending and drying of the concentrate

The concentrates are premixed during feeding to the feeding bins. Precipitates from the process are also mixed with the concentrates.

Preparation of primary feed mixture is carried out automatically by unloading the proper amount of feeding material from the feeding bins onto a belt conveyor. It is screened, crushed and the iron pieces are separated by a magnet separator before the mixture is conveyed to multicoil steam dryers, where it is dried to a moisture content of less than 0.2 % as required for flash furnace operation. Heat for drying is supplied by saturated steam. The off-gases from the dryers are cleaned in bag filters prior to discharge through the stack to the atmosphere. The dry feed mixture is conveyed to the flash smelting furnace feeding bins by a pneumatic conveyor.

2.4.3 Flash smelting

Dried copper concentrate feed mixture is fed by a loss-in-weight feeding system into the reaction shaft of the furnace through one concentrate burner. The mixing of gas and feed is effective and the concentrate particles react rapidly in suspension with oxygen in the hot reaction shaft. In older installations process air preheating of about 200–800°C was used in order to achieve an autogeneous reaction, but today in the majority of installations autogeneous operation is reached by using higher oxygen enrichment, 30–90 % of oxygen in process air. The degree of oxidation is controlled by the total oxygen/concentrate ratio and the temperature by the degree of oxygen enrichment. The smelting takes place in the reaction shaft without any external fuel addition, i.e. the chemical energy of the concentrate is utilised for smelting. Part of the sulphur is oxidised to form SO_2 and part of the iron is oxidised to iron oxides. The iron oxides and gangue form fayalite slag with the silica sand fed into the furnace in the feed mixture.

The reaction products from the reaction shaft are separated in the settler part of the furnace. Rich copper matte and slag separate further in the bath formed in the settler. They are tapped out of the furnace separately through tapping holes and launders. The fumes and SO_2 from launders are collected in hoods. Copper matte is further oxidised in converters to blister copper. It is then fed into the anode furnace for final oxidation and reduction before anode casting. The slag is cooled in large ladles and crushed and ground before flotation for copper recovery. The slag concentrate is fed into the Flash Smelting Furnace together with the primary concentrate. The remaining concentration sand is stable, because the remaining small amounts of metals are vitrified in the silicate matrix.

The fuel burners in the furnace are available to ensure furnace temperature during interruptions. The flash smelting furnace is provided with a jacket water cooling system. Warmed water from the cooling system is collected and led to cooling towers and then returned to the water tanks.

2.4.4 Gas cleaning

The fumes from slag and matte launders are collected in hoods and taken to tail gas scrubbing with alkalis. The gas produced in the reactions in the reaction shaft goes through an uptake shaft and is cooled in a waste heat boiler consisting of a radiation section followed by a convection section. The boiler is a forced circulation boiler, which produces saturated steam. Part of the dust settles in the waste heat boiler and the rest in the electrostatic precipitator. All of the dust is collected together and conveyed by a pneumatic conveyor into the flash smelting furnace flue dust bin for recycling.

Process gas fans are located after the electrostatic precipitator to maintain a slight underpressure in the furnace, waste heat boiler and precipitator and blow the process gases to sulphur recovery. The high sulphur dioxide content of the gas makes it possible to recover sulphur as liquid SO_2 and sulphuric acid.

There is a separate duct to carry the hot gases by-passing the waste heat boiler and electrostatic precipitator to the stack. This can be used during feed stoppages and other disruptions, when the gases can not be sent to the acid plant. Instead they are scrubbed before venting out through the stack.

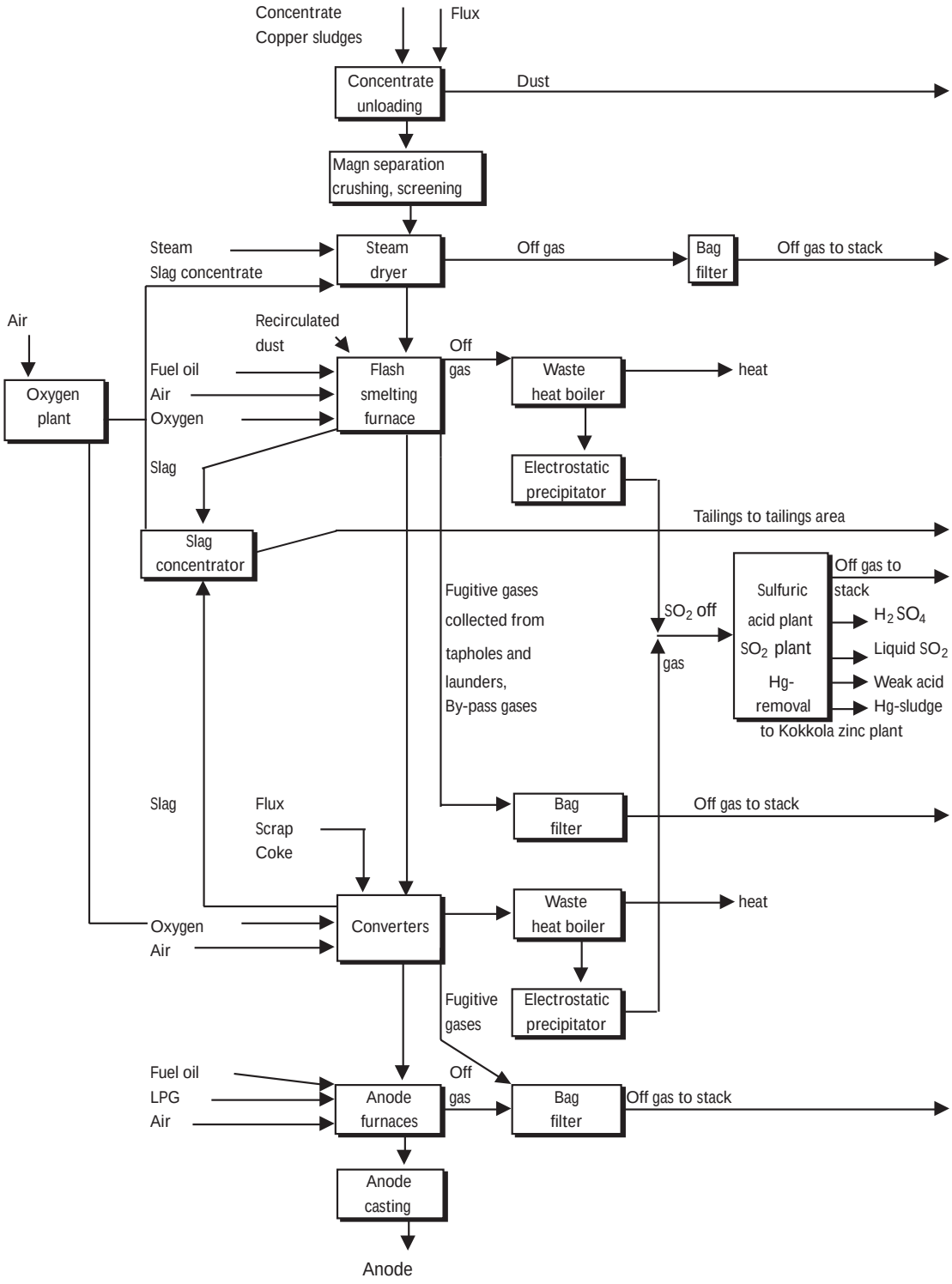

Figure 2. Flowsheet of the Harjavalta copper smelter.

2.4.5 Copper converting

The main raw material for converting is the molten Cu-Fe-S matte from smelting. The other raw materials are silica flux, coke and oxygen enriched air. Copper scrap can also be fed to the converter. Converting is done in a Peirce-Smith converter as a batch process. The oxygen enriched air is blown into the molten matte through submerged tuyeres. The process is autogeneous, the energy used is the chemical energy contained in the matte.

Converting is done in two stages. The first one is the slag-forming stage, in which iron and sulphur are oxidised. The converter is charged with matte in several steps, each step being followed by the oxidation of FeS from the charge. Slag is skimmed from the converter after each oxidation step and a new matte addition is made. The second stage is the copper making stage, in which the sulphur in the CuS_2 is oxidised to SO_2. The blister copper contains about 99 % copper.

The converters are driven by electric motors, but there are pneumatic-powered motors for the automatic emergency turnout. Turbo-type air blowers supply the process air to the converters.

The gas produced in the converter is taken through a tightly fitted hood system into a waste heat boiler, where it is cooled by generating steam from which the energy is recovered. After the waste heat boiler the gas is cleaned in an electrostatic precipitator and taken to the sulphuric acid plant. The dust recovered in the electrostatic precipitator is fed back into the Flash Smelting Furnace.

Fugitive gases from the converter hoods are collected by secondary hooding and treated by bag filter or one stage wet scrubbing with a desulphurising agent.

2.4.6 Slag flotation

The basic function of slag flotation is to separate copper from the slag by using flotation technology and to send the slag concentrate obtained back to the flash smelting furnace. This method offers an extra means of elimination of impurities in comparison to the electric furnace slag treatment where the matte formed is carried straight to converting.

The slag is cooled in large ladles, first slowly in the air and then by water jets for 1–2 days. During the cooling period the copper and matte particles grow and it becomes easier to separate them from the slag. After the cooling period the slag is crushed and ground. Copper recovery in flotation increases as the grinding degree becomes finer. Flotation is carried out in three steps in Outokumpu flotation cells. The slag concentrate slurry is pumped from the flotation cells to a thickener. The thickened concentrate is filtered with a pressure filter. Then the filter cake is conveyed to the dryer in order to be fed into the flash smelting furnace. The slag mill tailings are pumped to the tailing area nearby. The clarified water from the tailing pond is recirculated to be used as process water.

2.4.7 Copper refining and anode casting

Blister copper is refined in the anode furnace in order to remove the remaining sulphur and oxygen. The sulphur content of copper must be reduced to the level 0.005 % so that anodes with a smooth surface can be cast. In the first step sulphur is removed by blowing air into the furnace. As a result the oxygen content of the copper is 0.6–0.9 %. In the second step the extra oxygen is removed as gaseous carbon monoxide and water by injecting liquid propane gas to the molten copper until the oxygen content is 0.05–0.2 %. The refined blister copper is then cast into anodes. The Outokumpu-designed automatic anode casting system produces anodes of uniform shape, size and weight.

The spent anodes returned from electrorefining are conveyed to the converter where they are fed to the second stage of copper converting.

The anode furnace is covered by a movable hood construction. The furnace gases go through a bag filter to the stack.

2.4.8 Sulphuric acid plant

The gases from the flash smelting furnaces and the converters go through a dust elimination step and onto the sulphuric acid plant. The gases are mixed together and diluted, if necessary to the processing concentration 8.5–13.5 % SO_2.

The conversion rate of the double contact plants is higher than 99.7 %. The concentrated weak acid produced in the first gas washing stage is used in Outokumpu´s zinc plant in Kokkola and in the Pyhäsalmi mine. The Hg precipitate is also used in Kokkola, where Outokumpu has a mercury plant. Gypsum and inert precipitates are taken to a municipal landfill. The sales products from the acid plant are sulphuric acid, liquid SO_2 and energy.

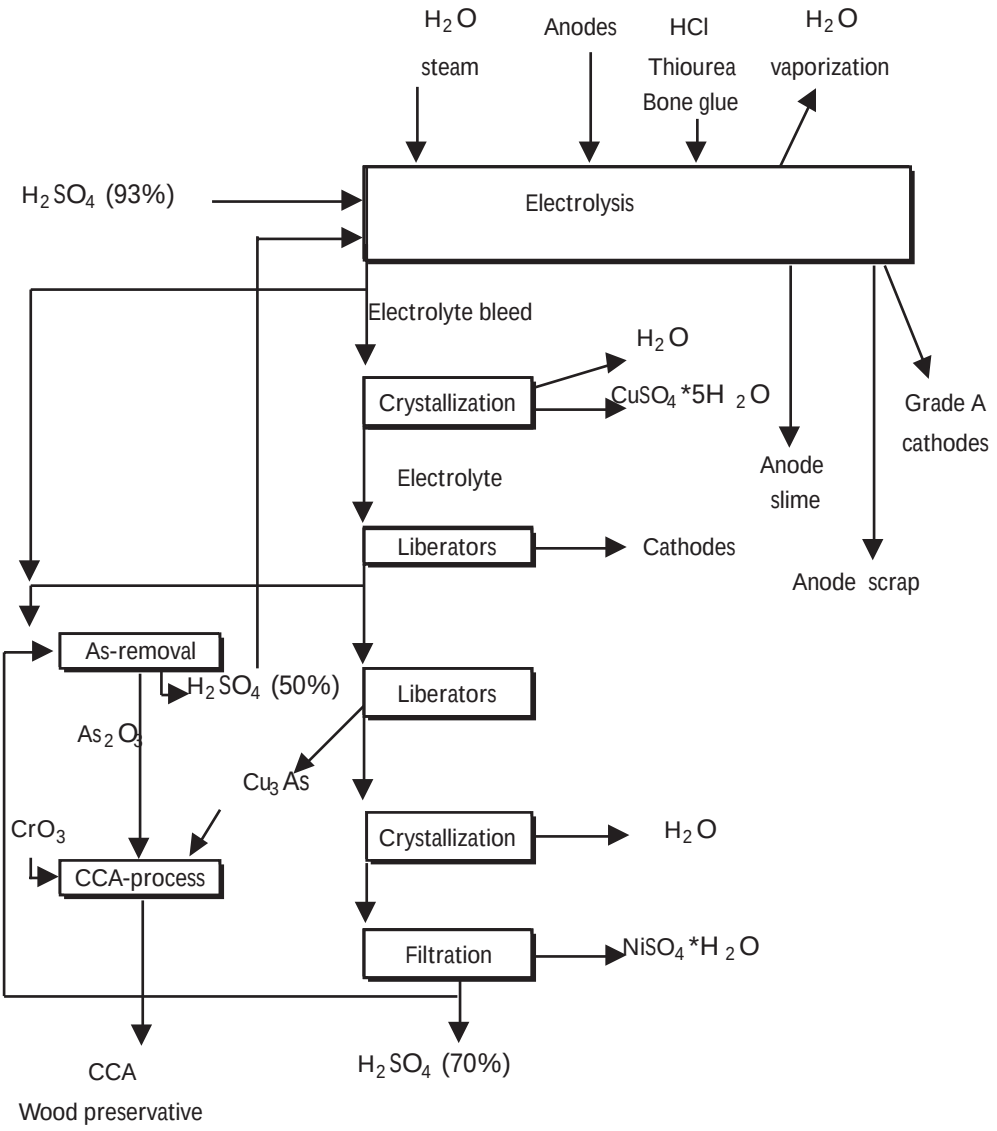

Figure 3. Flowsheet of copper electrolysis.

2.4.9 Copper electrolysis

The final refining of the anode copper is carried out in electrolytic cells in a tank house. Application of an electrical potential between the copper anode and a metal cathode in a $CuSO_4$-H_2SO_4-H_2O electrolyte causes the dissolution of copper from the impure anode and its deposition on the cathode. Some impurities are precip-

itated in the anode slime on the bottom of the electrolysis cells due to their insolubility in the electrolyte used. The dissolved impurities are taken in the bleed to solution purification (Figure 3).

The initial cathodes used are thin, pure-copper starting sheets, which are produced in the refinery itself. Fully grown cathodes are removed from the cells, washed with water and packed. They are sold for melting, casting and fabrication of copper semi products.

2.4.9.1 Solution purification in copper electrolysis

In the solution purification plant the impurities are removed from the electrolyte. To maintain the copper sulphate balance some of the copper sulphate is also removed by crystallisation and sold to customers.

From the copper sulphate crystallisation the electrolyte is conducted to a two-step copper electrolysis. In the first step the copper is removed from the solution as copper cathodes by electrowinning with insoluble lead anodes. These impure copper cathodes are returned to the smelter. In the second step arsenic is electrowon as copper arsenide precipitate on the copper sheets.

The solution obtained is taken to nickel removal. Nickel is crystallised as nickel sulphate in a vacuum evaporator. Nickel sulphate monohydrate is transported to Harjavalta to the Ni process.

The wood preservative CCA is manufactured from the copper arsenide which originates in electrolytic refining. CCA is a sales product and as such an excellent outlet for the arsenic in the process.

Elements nobler than copper form an insoluble anode slime which settles to the bottom of the electrolytic cells. The anode slime is led from the electrolysis to the Precious metal plant.

2.4.9.2 Precious metals recovery

The anode slime mainly contains elements electrochemically nobler than copper (Te, Se, Ag, Au, Pt, Pd). The slime slurry is pumped electrolysis to the Precious Metals plant. In the Outokumpu process the recovery of silver is 97 % and that of gold 99.7 %.

The slime is first leached in an autoclave at 170°C with 6–7.5 bar oxygen pressure in order to dissolve nickel, copper and tellurium. Tellurium is precipitated from the solution as copper telluride and sold (Figure 4).

2.4.9.2.1 Selenium

Selenium is recovered from the filter press cake in an electrically heated furnace where the temperature is around 400–600° C. Oxygen and SO_2 gas are used as reagents. Selenium compounds react at this temperature forming gaseous selenium dioxide. The selenium dioxide gas (SeO_2 (g)), is sucked from the furnace through the ejector into an aqueous solution (Figure 5). In this solution selenium dioxide is reduced to elemental selenium by sulphur dioxide at the temperature of 80°C. The selenium is commercial grade selenium (> 99.5 %). Selenium recovery is high. The selenium content of the roasted slime is normally around 0.5% /18–23/.

Due to the fact that the roaster is furnished with gas circulation devices, it offers homogenous atmospheric conditions throughout the roaster, which leads to nearly complete removal of selenium during the process. The outlets from the furnace are almost nil. The remaining aqueous solution is fed back to copper electrolysis.

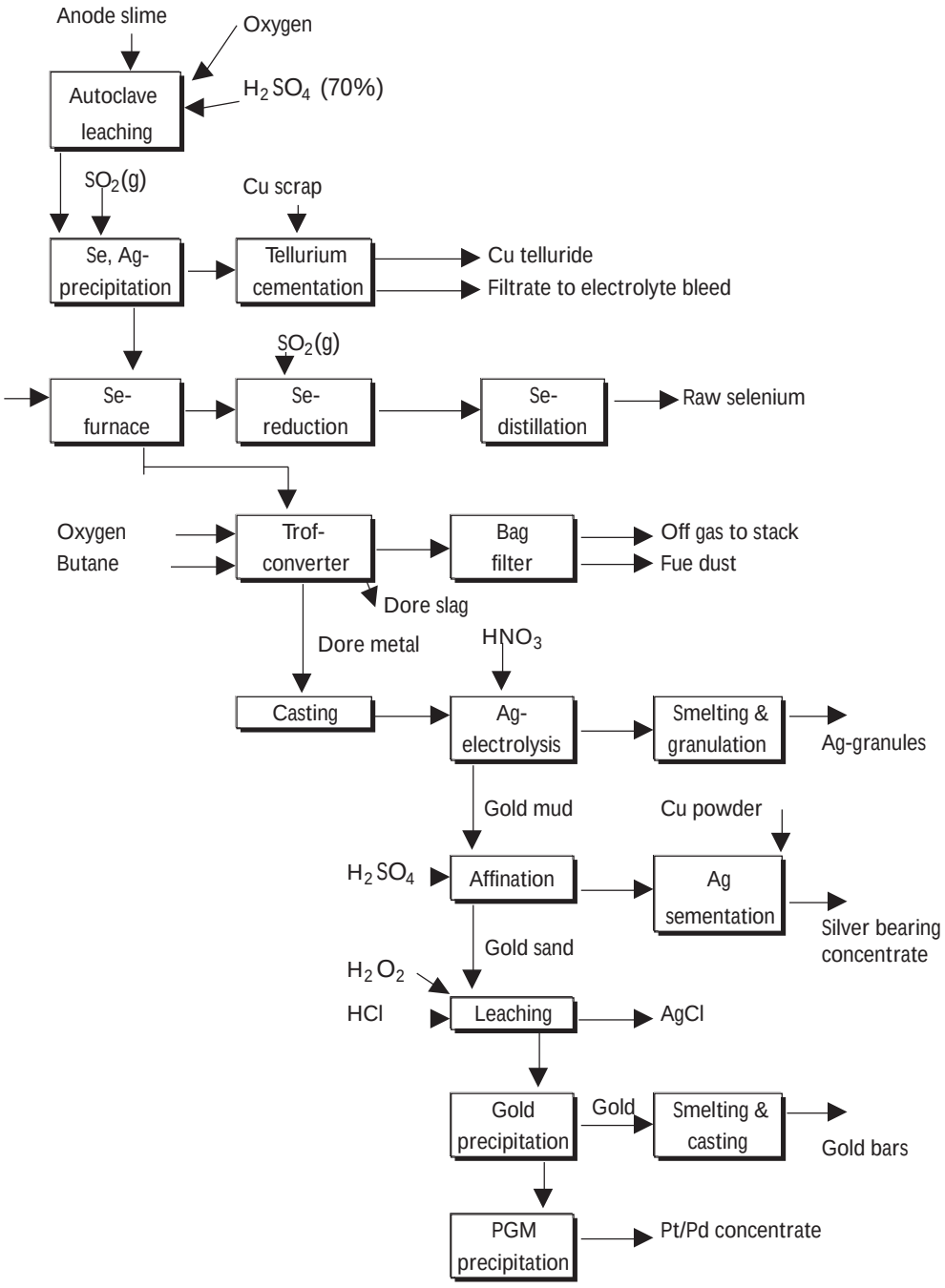

Figure 4. Flowsheet of precious metal recovery.

2.4.9.2.2 Silver

The deselenated slime is melted with fluxes to doré metal. After reduction the primary slag is removed from the furnace. The impurities (Te, Cu, Pb) are oxidised and the metal is cast to anodes. The doré metal contains mainly silver and gold, some platinum, palladium and small amounts of impurities. A secondary slag is produced in the oxidation stage. This slag is sold.

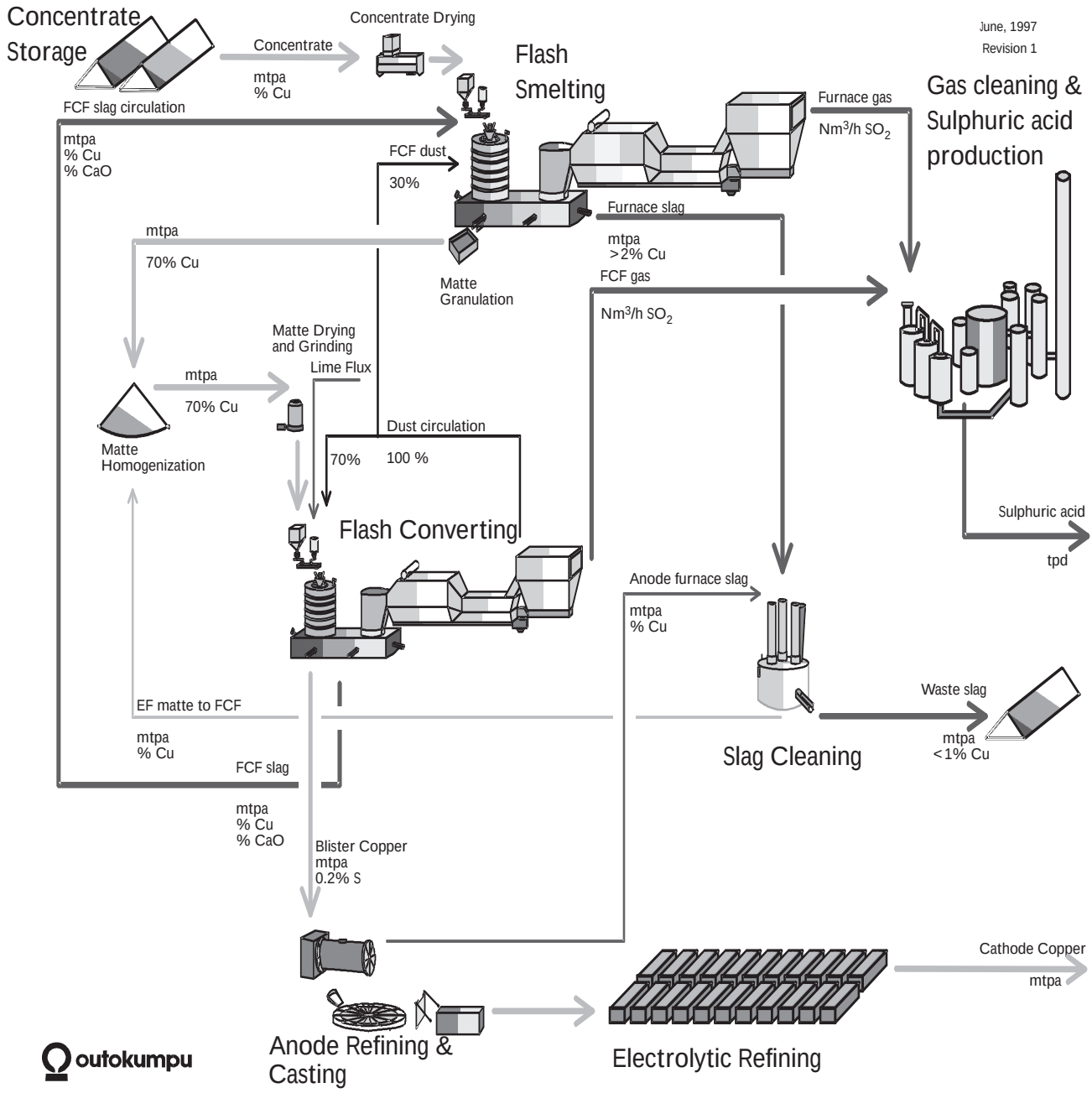

Figure 5. Copper production by Flash Smelting and Flash Converting.

The doré anodes are electrolysed to silver in aqueous silver nitrate solution. The silver crystals are deposited on cathodes. The elements which are not leached, like gold and platinum group metals, fall to the bottom of the anode-bags. The crystalline silver is melted at 1,300°C and granulated. The silver granules are dried, weighed and packed.

2.4.9.2.3 Gold

The slime from the anode bags is leached with hydrogen peroxide and hydrochloric acid to recover gold and platinum metals. Gold is reduced from the solution

by bisulphate and filtrated. The gold sand is melted and cast into gold bullions. The platinum group metals are recovered from the solution as Pt/Pd concentrate, which is sold as such.

2.4.10 Utilities and Off-Sites at the Harjavalta plant

2.4.10.1 Electric Power Supply

The main part of the electricity used is purchased from the public grid. The Outokumpu power plant produces electrical energy from the extra steam from the waste heat boilers of the flash furnaces and converters. This energy is used for in-plant heating and sold for district heating. Energy reduction and conservation techniques are prevalent throughout the plant.

2.4.10.2 Steam and Condensate System

The hot gases produced in the flash smelting furnaces and copper converters are cooled in waste heat boilers by generating steam. The steam formed is used in the drying of the concentrates, in the prewarming of the process air for the flash smelting furnaces and in the nickel process. The power plant produces electric energy from the extra steam.

2.4.10.3 Fuels Supply

All fuels used are supplied to the plant. Coke is stored in a storage building. The oil storage vessels are stored at the power plant. Propane is also stored in a storage vessel. Both oil and propane are distributed via their own pipelines to the various plants.

2.4.10.4 Oxygen Supply

On the site there are also oxygen and hydrogen plants. The three oxygen plants produce oxygen for smelting and at the same time some argon, which is sold.

The two hydrogen plants produce hydrogen for the nickel process. Hydrogen is also used in the purification of argon.

2.4.10.5 Process Effluent and Surface Water Treatment

All waste and rainwater is collected and pumped to reactors where all metals are precipitated with sodium hydroxide. The sludge formed is taken to clarification basins. The overflow is pumped to sand filters. The filtered water is discharged to the river. The sludge from the bottom of the clarification basin is pumped to a sludge basin. The settled sludge is transferred to a sand bed. The filled sand bed is dried and fed to the flash smelting furnace. The water overflows from the sludge treatment are collected in the rainwater basin, from which they are taken back to the beginning of the process.

2.4.11 Utilities and Off-Sites in the copper electrolysis at Pori

2.4.11.1 Electric Power Supply

The refinery has no power plant. Electricity is purchased from the public grid. Energy reduction and conservation techniques are prevalent throughout the refinery.

2.4.11.2 Steam and Condensate System

Steam is bought from the municipal power plant.

2.4.11.3 Fuel Supply

The refinery is connected to the main fuel gas pipeline of the copper-semis fabrication plant located on the same site.

2.4.11.4 Process Effluent and Surface Water Treatment

All process waters are in a closed circuit and no effluents are discharged from the copper refining plant. The surface waters are taken to the river which borders the refinery.

2.4.12 Commercial Quality Control and Process Control Laboratories

There is a well-equipped modern analytical laboratory in Harjavalta. It has three assay teams, the first one for commercial assays, the second one for product assays and the third one for process and environmental assays. The sampling team supplies representative samples to the laboratory.

In the copper refinery in Pori there is a small laboratory for analysing some of the local process samples. Other process samples are sent to Harjavalta.

2.5 Outokumpu Flash Converting

High grade matte is granulated directly from the flash smelting furnace without any ladle transport (see Figure 5). Thus the revert formation rate and the emissions to the working atmosphere are low. Granulated matte is ground and simultaneously dried in a roller mill before feeding into the flash converting furnace.

Copper matte is smelted with oxygen enriched air (65–75 % O_2) in the flash converting furnace in which the chemical energy of the matte is used in order to produce molten blister copper and slag. The dust can be recirculated back into the flash converting furnace or into the flash smelting furnace in order to recover the valuable materials in the dust.

The same chemical energy contained in the matte that is used in conventional Peirce-Smith converting is also utilised in flash converting. The reactions in the shaft are mainly exothermic. Most of the time both flash smelting and flash converting furnaces are able to operate autogenously with high oxygen enriched air only, without external fuel for smelting. High oxygen enrichment in both furnaces also means that the gas volume leaving both furnaces is low and therefore the investment costs of gas cleaning are also low and high sulphur recovery is possible.

In the reaction shaft the matte particles are heated rapidly and they ignite. The oxidising reactions therefore proceed very fast. Metallic blister copper and slag

separate in the settler part of the furnace. The blister copper is tapped from the flash converting furnace via launders directly into the anode furnace. The slag is granulated before feeding back into the flash smelting furnace for the recovery of valuable material. One option is to return the slag in molten form to the flash smelting furnace. Both blister and slag launders are covered by a hood in order to collect fugitive emissions and SO_2.

Process gas, rich in SO2, flows continuously through cooling and cleaning steps to the sulphur recovery plant. Sulphur recovery can be over 99.9 %.

As the two smelting processes are not directly connected together, it is possible to operate one furnace even if the other is not operating. This ensures high on-line availability for the whole process /3-14/.

2.6 Outokumpu Direct Blister Smelting

Copper concentrates containing over 35 % copper or special low iron concentrates can be economically treated by the Direct Blister Flash Smelting Process. Suitable concentrates can be made from chalcocite or bornite-chalcocite ores, which have high copper contents or whose copper/iron ratios are high compared to chalcopyritic concentrates.

A dried copper concentrate feed mixture is fed into the reaction shaft of the flash smelting furnace through one concentrate burner. The mixing of gas and feed mixture is effective and the concentrate particles react rapidly in suspension with oxygen in the hot reaction shaft. The smelting takes place autogenously in the reaction shaft without any external fuel addition, i.e. the chemical energy of the concentrate is utilised for smelting. Sulphur is oxidised to form SO_2 and iron is oxidised to iron oxides. The iron oxides form fayalite slag with the silica sand fed into the furnace in the feed mixture.

The reaction products from the reaction shaft are separated in the settler part of the furnace. Blister copper and slag separate further in the bath formed in the settler. They are tapped out of the furnace separately through tapping holes and launders. The fumes and SO_2 from the launders are collected by hoods. Blister copper is then fed into the anode furnace for final oxidation and reduction before anode casting. Copper in the slag is recovered in an electric slag cleaning furnace. The waste slag from the slag cleaning furnace is stable because the small amounts of metals left are vitrified in the silicate matrix.

The gas produced in the reactions in the reaction shaft goes to a waste heat boiler, where it is cooled by generating steam from which the energy is recovered. After the waste heat boiler the gas is cleaned in an electrostatic precipitator and routed to sulphur recovery. The high sulphur dioxide content of the gas makes it possible to recover sulphur as liquid SO_2 and sulphuric acid. The dust recovered in the electrostatic precipitator is fed back to the Flash Smelting Furnace /15-17/.

2.7 Hydrometallurgical Copper Production

The research done to develop leaching processes for sulphide concentrates has resulted in much being learnt about the ways in which sulphide minerals react and it has been recognised that there are marked differences in the stability and ease of dissolution of various sulphides. Amongst the copper sulphide minerals, chalcocite, Cu_2S, is the easiest to dissolve and chalcopyrite, $CuFeS_2$, the most abundant copper mineral, is the most refractory and difficult to leach.

Of the many processes that have been proposed for the hydrometallurgical production of copper, the majority have been developed only as far as bench scale,

a few have reached pilot scale and only three have been commercialised. The Clear and Arbiter processes operated for only a few years and proved to be commercial failures, primarily because they were not able to produce copper of a high enough quality at a competitive price.

The Escondida process has been in use for some years. It is an ammonia leach to dissolve one copper from Cu_2S and leave CuS undissolved. Dissolved copper is turned into metallic copper by solvent extraction-electrowinning. CuS is concentrated and melted. The plant was, however, closed in spring 1998 due to low copper prices.

2.7.1 Copper heap leaching

The most common way to process copper sulphide ores, the flotation-smelting-refining process, accounts for over 80 % of global copper production. The hydrometallurgical route, leaching-solvent extraction-electrowinning, is expected to account for 20 % of world copper production by the year 2000. The figure consists mainly of oxide copper ores (azurite, malachite, tenorite, chrysocolla, brochantite, enargite), but has recently been expanded to include sulphide ores (chalcocite, covellite, bornite). The leaching of sulphide ores is catalysed by common iron and sulphur oxidising bacteria /24,25/. The copper heap leaching flowsheet is shown in Figure 6.

The main minerals leached on industrial scale today are porphyry copper ores. Most of these ore deposits can be mined as low cost open-pit mines because of the geology of these mineralizations. The ore preparation, ore placement, heap design, solution application and solution management are usually designed considering the specific ore type, the local geology and climate.

2.7.1.1 Crushing

The heap leaching of copper normally requires a comminution step. This achieves the desired size range to optimise copper recovery and long-term ore permeability. The size of the crushed product is normally between 6 and 20 mm depending on the ore type. One limit imposed on the fines content has been a maximum of 10 to 15 %–100 mesh. A bigger fines content reduces the ore permeability in heap leaching and subsequently the ultimate copper recovery.

Crushing has three stages where the last stage, tertiary crushing, uses the water flush technique. Ore is fed to the primary crusher and the discharge feeds the adjacent secondary cone crushers. Crushed ore is then conveyed to a stockpile. From the stockpile the ore is fed to tertiary water flush crushers. After tertiary crushing the ore pulp is screened with double deck screens. The oversize is recycled to crushing and the intermediate size is fed to heap leaching. The cyclone slime is thickened and the underflow is transported by gravity to the disposal area.

Dry crushing has been furnished with an effective dust collection system, which takes the dust back to the process after agglomeration with moisture.

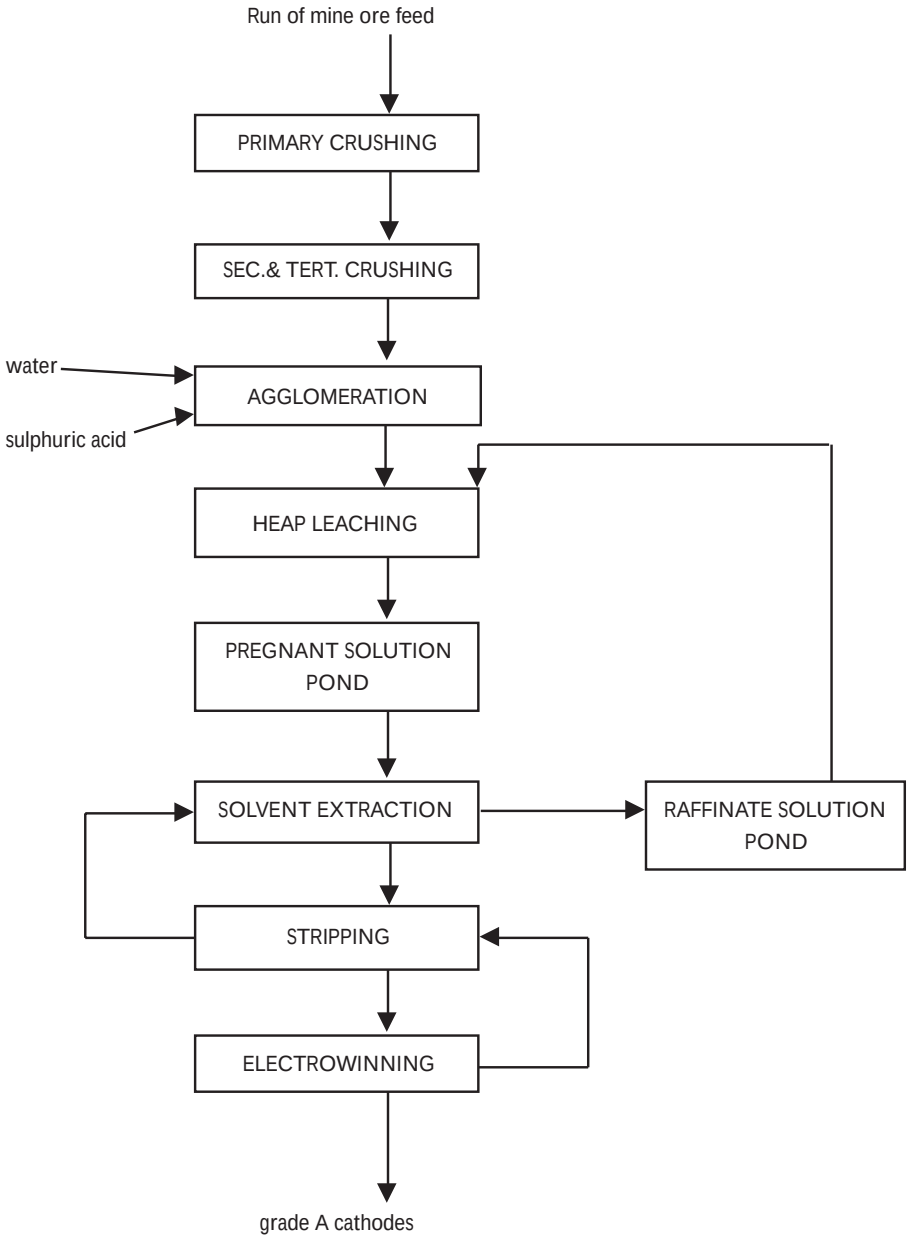

Figure 6. Flowsheet of the copper heap leaching process.

2.7.1.2 Agglomeration

The crushed ore is agglomerated with sulphuric acid and water in a rotating drum. In order to get good agglomerates with crushed ore a wetting medium is needed. This can be water or raffinate solution. If the ore is sulphide ore, raffinate or a bacterial inoculum is used in order to get the bacteria evenly distributed throughout the whole heap. Agglomeration binds the fine particles to the surface of the coarser particles, passivates the silicate surfaces and lowers the concentration of impurities in the pregnant leaching solution. After agglomeration the ore is left to rest, "to cure", for at least 24 hours. During this period the solvent will start to attack the ore making the leaching period shorter and easier.

2.7.1.3 Heap building

Oxide and sulphide ores are stacked and leached separately due to different requirements in their leaching behaviour. The base of the leaching area is levelled, compacted and covered with an HDPE lining. The inclination of the base is 5 % towards the collection ditch of the pregnant leaching solution. The main draining pipes are placed at 6 metre intervals from each other directly on the liner. The aeration of sulphide heaps is provided by pipes put every six meters in the heap bottom to permit oxygen flow for the bioleaching.

The transportation of the ore to the oxide or sulphide heap leach area is performed by overland conveyors. The stockpiling of the heaps is done by grasshopper conveyors and radial stackers. The sulphide ore is stacked in 6 metre high lifts and the oxide ore in 8–12 m lifts.

The leaching solution is applied on top of the heap by drippers. They are placed on a grid pattern of 0.8 by 1 m. The raffinate solution from the solvent extraction plant is pumped to large headers running the length of the heap. Secondary headers carry the solution to the top of the heap. The solution is applied at the rate of 5–10 l/h/m^2.

2.7.1.4 Heap leaching

The raffinate solution from solvent extraction is applied to the top of the heap by drippers at a rate of 5–10 l/h/m^2. Irrigation is continued until the copper concentration in solution falls under a pre-estimated value i.e. 0.5 g/l. The leaching time for oxide ore is normally from 50 to 100 days. Sulphide ore needs a much longer time, about 300 days.

The difference between the leaching mechanisms of oxide and sulphide copper ore is that the oxide ore is only leached with protons (H^+), but sulphide ores need oxygen, protons (H^+) and active bacteria (*Thiobacillus ferrooxidans, Thiobacillus Thiooxidans, Leptospirillum ferrooxidans* etc.) The main point in the leaching of oxide copper ore is proper irrigation and wetting of particles inside the heap, but the leaching of sulphides needs enough dissolved air in the leaching liquor and correct living conditions for the bacteria, e.g. temperature, pH, nutrients, oxygen and carbon dioxide.

2.7.1.5 Solvent extraction

In the solvent extraction process for copper the solution purification stage after leaching is carried out by a liquid-liquid extraction process. In the first stage copper is selectively extracted from the pregnant solution to the organic phase. In the second stage, copper is selectively stripped from the organic phase to the aqueous electrolyte, which is then routed to electrowinning.

In the liquid-liquid extraction process the separation of the different phases is very important in order to be able to produce high grade copper in the electrowinning process and to avoid organic phase reagent losses into the leaching process. The solution in the Outokumpu VSF (Vertical Smooth Flow) process to this is that pumping and mixing are separated. With a sophisticated pumping device (DOP, Dispersion Overflow Pump) and a helical, low shearing stirrer the droplet size of the dispersed phase can be maintained ideal for copper mass transfer between the phases. At the same time the formation of small droplets and an emulsion can be avoided. In addition, the specific energy consumption of the whole mixer-settler is lower than in conventional processes.

After the dispersion stage the phases are separated in a newly designed settler, which makes it possible to reduce the settling time i.e. to increase the specific

flow rate of the process unit and still to obtain a clear product solution from the copper solvent extraction circuits.

Smooth mixing of the phases also prevents the contact of oxygen in the air and the organic phase. This prevents the loss of organic reagents by degradation and also reduces crud formation in the process. The tendency for crud formation as well as reagent degradation are further reduced by covering the process units so that dust cannot settle in the process units. This also reduces the chance of volatile organic carbon emissions to the environment from the organic phase.

The process is able to operate in variable conditions. Normally the temperature at leaching-solvent extraction-electrowinning plants varies a lot depending on the time and date. However, the variable speed pumping and mixing are able to respond to the variations of viscosity caused by temperature changes as well as flow rate variations /62-67/.

2.7.1.6 Electrowinning

Stripping the loaded solvent produces a relatively small volume of aqueous solution, typically containing 40–50 g/l copper with low levels of impurities. This solution is pumped to the tank house for electrowinning.

Electrowinning is the final stage in the production of copper in the leaching-solvent extraction-electrowinning process. The acidic copper sulphate solution is passed through cells in which insoluble anodes (positive) and cathodes (negative) are suspended. The anodes are made from a lead, tin and calcium alloy and the permanent cathodes are made of stainless steel. The reaction occurring in the cell is:

$$CuSO_4 + H_2O \text{ —> } Cu + H_2SO_4 + 0.5O_2 \quad (1)$$

The regenerated acid, containing about 20–30 g/l copper, is recycled to the solvent extraction plant to be used as stripping solution. Oxygen is released at the anode.

About once a week the cathodes are removed, washed and the copper is stripped using automated stripping machines, which sample, weigh, mark and strap the cathodes in bundles of 2.5 tonnes ready for the market.

3 Present Consumption and Emission Levels

3.1 Present Consumpion Levels

3.1.1 Energy consumption

The energy consumption used in copper production in Harjavalta was as follows in 1996:

3.1.1.1 Copper smelting from concentrate to anodes

Production capacity 160,000 t/a, capacity utilisation 94 %

oil	50–70	kg/t Cu
electricity	500–700	kWh/t Cu
natural gas	30–60	Nm^3/ t Cu
coke	30–50	kg/t Cu
oxygen	700–800	kg/t Cu

3.1.1.2 Copper refining

Production capacity 130,000 t/a, capacity utilisation 96 %

electrical energy	320–390	kWh/t Cu

3.1.1.3 Energy recovery

The hot gases produced in the flash smelting furnace and copper converters are cooled in waste heat boilers by generating steam from which the energy is recovered. The steam formed is used for example in the drying of concentrates, in the pre-warming of the process air from the flash smelting furnace and in the nickel process. Electricity is made from the extra steam in the power plant. In 1996 389,640 t of steam was regenerated from the waste heat boilers. 52,230 MWh was sold as district heat and 32,230 MWh was used for the heating of the plant and workers houses.

3.2 Environmental Emissions

3.2.1 General

The main environmental issues in the refined copper producing industry are air and water pollution and the generation of hazardous wastes. In general, copper plants have their own water treatment plants. This chapter describes emissions and abatement techniques for air and water pollution as well as waste production and treatment in the Finnish copper industry.

Outokumpu produces copper and nickel at its Harjavalta plant. Both production processes use the Outokumpu flash smelting technique and use sulphidic concentrates in this integrated process. The main end products are anode copper,

electrolytic nickel and nickel powder. The emissions to air and water measured are a result of this integrated process. The only way to get data on the copper process is to divide the emissions by the ratio of the copper and nickel produced.

The copper anodes produced are refined to cathodes at the Pori plant situated 30 km from Harjavalta. The Pori plant consists a copper refinery, foundries and copper semi-products fabrication. The emissions to water measured are again results from the whole plant.

The production values for 1997 were:

Cu anodes	159,300 t
Ni	35,300 t
H_2SO_4	580,200 t
SO_2 (liquid)	35,900 t
Cu cathodes	116,300 t
Au	3,900 kg
Ag	32,200 kg
Se	43,200 kg
$NiSO_4$	900 t
$CuSO_4$	3,200 t
Pt-, Pd-concentrate	450 kg
CCA wood preservative	1,740 t
Cu telluride	4,200 kg

3.2.2 Emissions to air

The emissions to air consist of particulate matter and SO_2. Sulphur dioxide gas comes from the flash smelting furnace and converters. It is routed to the sulphuric acid plant. Dust is formed whenever the concentrate is handled, during concentrate unloading, steam drying, in the flash smelting Furnace, in the converters, in the anode furnace and in the slag concentration plant. All these dust-containing gases are routed through bag filters to the stack. All collected dust is sent back to the flash smelting furnace.

The sources of dust and sulphur dioxide are shown in Table 5.

Table 5. Relevance of components with respect to air pollution.

Emission source	Dust and metal compounds	Sulphur dioxide
Material handling	relevant	not relevant
Storage	relevant	not relevant
Drying	relevant	relevant
Scrap treatment	relevant	not relevant
Smelting	relevant	relevant*
Slag treatment	relevant	not relevant
Ladle transfers	relevant	not relevant
Converting	relevant	relevant*
Fire refining	relevant	not relevant
Anode casting	relevant	not relevant
Electrorefining	relevant	not relevant
Sulphuric acid plant	not relevant	relevant

** the emissions from the smelting and converting stages are treated in the gas cleaning steps and the sulphuric acid plant; the remaining emissions of sulphur dioxide from the sulphuric acid plant are still relevant.*

Beside these process emissions, components will also be emitted diffusely. This can lead to locally enhanced concentration levels. The abatement of this fugitive emission is an ongoing process and demands good housekeeping. Possible measures include better sealing of equipment, forced ventilation combined with bag filters etc.

3.2.2.1 Sulphur dioxide

Sulphur dioxide can be emitted from the primary feed preparation and drying stages but the amount is usually very low so that simple gas scrubbing is adequate. The most significant sources of sulphur dioxide are the smelting and converting stages. The sealed Flash Smelting Furnace allows the sulphur dioxide to be collected. The oxygen enrichment used produces a high sulphur dioxide concentration with minimal variations in concentration. This therefore allows efficient conversion to sulphuric acid in the double contact sulphuric acid plant.

The conversion stage using the Peirce-Smith converter also produces a significant concentration of sulphur dioxide. It is not as well sealed as the smelting stage. The feeding and transfer of matte is a significant source of fugitive fumes. The sulphur dioxide concentration in the gases varies significantly depending on the stage of the conversion. Several converters are therefore used in a phased sequential operation and the off-gases are combined to reduce this effect. These gases are mixed with the steady, more concentrated gases produced by the Flash Smelting Furnace to maintain steady conditions in the sulphuric acid plant.

After heat recovery and cleaning in electrostatic precipitators the gases are mixed together and diluted, if necessary, to the processing concentration of 8.5–13 % SO_2. One source of sulphur dioxide emission is also the sulphuric acid plant, where the gas is converted with an efficiency of 99.7 % to sulphuric acid in the double absorption process.

3.2.2.2 Dust and dust-bound metals

These can be emitted from most stages of the process. Direct and fugitive dust emissions from the smelting, converting and refining stages are potentially high. The significance of the emissions is also high as these process stages are used to remove volatile metals such as Zn, Pb, As, Cd and Hg from copper and these metals are present in the dust. The Flash Smelting Furnace is effectively sealed to minimise fugitive emissions. Good maintenance of the furnace and ducts is practised and the gases are treated in dust removal systems and a sulphur recovery process.

The conversion and fire refining stages are not as well sealed as the smelting stage. The feeding and transfer of matte is a source of fugitive fumes. More importantly the use of the ladle transfer system is a significant source of fume and also inhibits the effectiveness of the fume collection hoods with the Peirce-Smith converters.

Electrolysis aerosol emissions take place in the hall. These emissions leave the hall via natural ventilation. Metal aerosols from electrolysis are considered to be relevant.

The main emissions from the copper refinery come from the precious metals plant. In the selenium furnace the selenium dioxide gas is sucked from the furnace through an ejector into an aqueous sulphuric acid solution which is recirculated in the process. Some SO_2, selenium and dust is emitted through the exhaust air tube from the recirculated solution tank. The emissions are taken to the precious metals plant stack.

The deselenated slime is melted in the Trof converter. The gases from the furnace and its environment are taken to bag filters. Some SO_2, selenium and dust penetrate through the filter membrane.

The third possible emission from the precious metal plant comes from the preparation of silver nitrate when silver granules are dissolved in nitric acid. The NO_x-fumes are wet scrubbed from the gas phase.

3.2.3 Legislation and regulation in Finland

Finland has no single environmental law at the moment. Environmental legislation is composed of a number of individual acts /27/. A new Environmental Protection Act is currently under preparation and will combine the environmental acts according to the requirements of the Council Directive 96/61 /EC of September 1996 concerning integrated pollution prevention and control (IPPC).

Presently, the integrated approach is included in the two separate permit procedures: the environmental permit procedure, according to the Environmental Permit Procedure Act (735/1991) and Decree (772/1992) and the water discharge permit procedure, according to the Water Act (264/1961) and Decree (282/1962).

The Environmental Permit Procedures Act combines the permit procedures of the Air Pollution Control Act and Decree, the Waste Act and Decree, the Health Protection Act and Decree and the Adjoining Properties Act. The competent authority in environmental permit matters is, depending on the line of activities, either the Regional Environment Centre or the local environmental board.

When discharging waste waters, the Regional Environment Centre must be notified in advance regarding any plans for the discharge of wastewater in the cases listed in the Prior Notification Decree. The Centre assesses the notification and judges whether the activity will cause water pollution. If pollution is unavoidable, the polluter must apply for a permit from the Water Court or from the local environmental board. Substantial polluters send their applications directly to the Water Court. Polluting of groundwater is totally forbidden; this means that no permit can be granted for discharging pollutants into the groundwater.

In the metallurgical industry, an environmental permit granted by the Regional Environment Centre and a water discharge permit granted by the Water Court are needed.

Although the environmental legislation is based on a sectoral approach, the permit system in each sector follows certain uniform lines including the following elements (both in environmental and water permit matters):

- An application describing the activity and its environmental effects is to be submitted to the competent authority. The data and information that the operator of an industrial plant (the applicant) has to submit in the form of an application to the authority is prescribed in the above mentioned Acts and Decrees.
- The documents are public and the persons and organisations affected by the project have a right to comment on them.
- The competent authority makes a decision including emission limits and other permit conditions.
- Those concerned have the right to appeal against the decision.
- A revision of the decisions and permit conditions is made by a certain deadline stipulated in the permit (3-10 years where wastewater discharges are concerned) or when there are significant changes in operation or emissions or when unexpected effects are detected.

Right at the preliminary stage of planning a new establishment, the necessary permits and environmental aspects are to be surveyed. The enterprise is expected

to recognise that the environmental criteria may affect siting as well as other economic and technical decisions. Even in the case of changing the production, raw materials or technical devices at an existing plant, the authorities must be informed as soon as these decisions are made, and negotiations shall be initiated to survey the possible need for renewing the permits.

The legislation is based on the Polluter Pays Principle in the sense that the polluter pays all pollution abatement costs, which also include the monitoring costs. In addition, polluters of watercourses are obliged to pay indemnities to the owners of water and shore areas as well as to professional fishermen for any damage caused. A typical feature of the permit procedure is the case-by-case consideration of applications and tailor-making of the permit conditions. The permit conditions are expressed as emission limits and compulsory measures and not as technical standards.

3.2.4 Emissions to air at Outokumpu Harjavalta Metals

The ambient air concentrations allowed by the authorities for the whole integrated Harjavalta plant, which produces both copper and nickel, (the permit in force was granted 27.2.1995) are as follows:

3.2.4.1 SO_2

1. SO_2 concentration (mean value during an hour) in open air has to remain under 250 µg/m^3 after 31.12.1999 and the mean value during 24 hours must remain under 80 µg/m^3. From the hourly means not more than 1 % can exceed the value 250 µg/m^3 during 30 days and from the daily means 1 can exceed the value 80 µg/m^3 during 30 days.
2. If the SO_2 concentration is exceptionally high or exceeds 250 µg/m^3 the reason for the high value must be found out immediately.
3. If the SO_2 concentration exceeds 1000 µg/m^3 during three consecutive hours, the emissions have to be further restricted.
4. After 1.1.1997 the sulphur emissions from the sulphuric acid plant must not be more than 2.7 kg/ton of 100 % sulphuric acid produced calculated as a mean of six months.
5. The oil fuels used must not contain more than 1 weight-% of sulphur. This does not concern use in places from which the gases are routed to the sulphuric acid plant.
6. After 1.1.1997 the total emission of sulphur compounds calculated as SO_2 must not exceed 4500 t/a.

3.2.4.2 Dust

7. The dust separation system in the drying of copper and nickel concentrates must be such that the dust content of the gas does not exceed 10 mg/m^3.The bag filters used for the gas coming from the smelters, converters and anode furnace must be designed in such a way that the dust content after the filters does not exceed 1 mg/m^3.
8. Dust emissions from the power plant must not exceed 40 mg/MJ.
9. The total dust emissions from the plant must not exceed 90 t/a after 1.1.1997.

10. After 1.1.1997 the heavy metals and arsenic emissions must not exceed the following limits:

Cu	12 t/a
Ni	5 t/a
Zn	10 t/a
Pb	5 t/a
As	2 t/a
Cd	0.5 t/a
Hg	20 kg/a

3.2.5 Off-gas monitoring

In Harjavalta the emissions to air are measured from all stacks where emissions are significant. The dust emissions are measured once a month for 1–2 weeks from all the stacks after the filtering devices. The SO_2 emissions and the gas flows are measured continuously from the stacks. The results are registered in the local network.

In Pori Outokumpu Research Oy performs the air emission measurements according to the monitoring program defined in the licence for the Pori site. Outokumpu Research has a certified quality system according to the SFS-ISO 9001 standard. The SO_2, dust and metals concentration and mass flow measuring methods have been accredited by the Centre for Metrology and Accreditation according to the standards SFS-EN 45001 and ISO/IEC Guide 25.

3.2.6 Releases into air

Actual sulphur dioxide emissions at the Harjavalta plant in 1997 are presented in Table 6. The total volume of gas at the Harjavalta plant is 1,700,000 Nm^3/h, from which 1,000,000 Nm^3/h goes through the filters. The amount of gas from the sulphuric acid plant is 200,000 Nm^3/h.

The SO_2 concentrations in the ambient air have been measured from three places in the vicinity of the plant. The values measured have been low. The concentrations have been much lower than the limit values.

The design values for the bag filters have been 1 mg dust/Nm^3. With the new bag filters installed the actual emissions were lower than the limit values in 1995. During the next two years there were difficulties with the filters and the limit values were not reached. This year, 1998, the matter has been brought under control.

The air emissions in the Pori copper refinery in 1997 are presented in Table 8. The only permit condition given to the copper refinery is the amount of selenium in the precious metals plant off-gases, which must be under 300 kg/a.

Table 6. Sulphur dioxide emissions at Harjavalta in 1997.

	Height of stack	Area	t/a 1997	specific emission
Smelter ventilation gases	140 m	Converters	1 066	
		Smelting furnaces	1 176	
		Sum	2 242	16 kg SO_2/t metal (Cu + Ni)
Off-gases from sulphuric acid plant	140 m	R6	229	1.6 kg SO_2/t H_2SO_4
		R7	294	0.7 kg SO_2/t H_2SO_4
		Sum	523	
Dryer stack	70 m	Ni-dryer	57	
		ventilation gases	11	
Cu drying	40 m		0	
Fugitive gases			147	
Sum			2 980	

Table 7. Dust and metals emission to air in 1998.

	Limit t/a	t/a in 1998	Specific emission
Dust	90	72	0.37kg/t metal (Cu + Ni)
Cu	12	12	0.08 kg/t Cu
Ni	5	1	0.03 kg/t Ni
Zn	10	5	
As	2	2	
Pb	5	2	
Cd	0.5	0.4	
Hg	0.02	< 0.02	

Table 8. Air emissions in the copper refinery in 1997.

	t/a 1997	specific emissions
SO_2	33	0.28 kg/t Cu
dust	0.08	0.0007 kg/t Cu
Se	0.1	0.008 kg/t Cu
As	0.7	0.006 kg/t Cu
NO_x as NO_2	0.4	0.003 kg/t Cu
CO_2	316	2.7 kg/t Cu

3.2.7 Emissions to water

Effluenst to the waterways contain process waters from the acid plant and a bleed of the water used in the slag concentrator, cooling waters, e.g. the water used to cool the anodes, circulating via cooling towers and surface drainage. All these waters are collected and treated in the water treatment plant. The cleaned waters are discharged to the river which flows by the side of the plant. The precipitates are sent back to the flash smelting furnace. Some of the sewage water from the plant is taken to the municipal purification plant. Cooling water and process waters are recycled within the process as long as possible.

3.2.7.1 Suspended solids and metal compounds

These can be emitted from most stages of the process. Surface water can result from either rainfall or from the wetting of stored material to prevent dust formation. The other potential source of suspended solids and metal compounds are the cooling

and granulating steps. In general these systems are either sealed and the water is recirculated or they are not in contact. System leakage can occur. Wash waters, spent electrolyte and process effluents are also produced in the tank house and scrubbers. These effluents contain significant quantities of metal compounds in solution and are treated along with liquors bled from the sealed cooling and granulating systems before discharge to the waterways.

Sludges from all possible processes are usually returned to the flash smelting furnace in order to recover their metallic portion. In the mercury removal step in the sulphuric acid plant the circulating acid in the drying towers is treated with thiosulphate to precipitate mercury. The precipitate is taken to the company's mercury plant in Kokkola.

The main water emissions from the copper refinery come from the condensing water of the air-conditioning. It contains small amounts of copper and sulphuric acid. The selenium granulating water contains an amount of selenium which is hardly measurable. The remainder of the gold process contains some hydrochloric acid, but it is nowadays added to the electrolysis as a chloride addition. Some surface drainage comes from the refinery, too.

The permit conditions for Harjavalta (permit of Water Rights Court 31.12.1992) are as follows. The process waters must be cleansed in such a way that the effluents released from the plant do not contain more than:

Cu	3.6 t/a	(= 10 kg/day)
Ni	3.6 t/a	
Zn	3.6 t/a	
As	1.8 t/a	
Pb	1.08 t/a	
Cd	0.108 t/a	
Hg	0.010 t/a	

3.2.7.2 Waste water monitoring stations

At both Harjavalta and Pori, the drain system outlets are equipped with flow measuring and sampling stations. Temperatures and pH are also measured on a continuous basis. Flow measurements are done using electromagnetic flowmeters. Flow, pH and temperature readings are registered into the plant control system. Sampling is done proportionally to the flow. Composite samples are taken for analysis every day.

3.2.7.3 Analysis and reporting of waste waters

The analytical laboratories in Harjavalta and Pori analyse the necessary metal compounds from the daily composite samples. Results are reported internally via local networks. Both laboratories are covered by the plants' ISO 9002 certificates.

3.2.7.4 Effluents in 1997

The emissions to water at Harjavalta in 1997 are shown in Table 9. The total water flow was 31,000,000 m^3/a including cooling waters.

Table 9. Actual emissions at the Harjavalta plant in 1997 were:

	Limit t/a	t/a 1997	Specific emission
Cu	3.6	3.6	0.023 kg/t Cu
Ni	3.6	4.4	0.124 kg/t Ni
Zn	3.6	1.7	
As	1.8	0.4	
Pb	1.08	0.17	
Cd	0.11	0.06	
Hg	0.01	0.01	

The high nickel values were due to heavy rains, which washed dust from the yards to the waste water treatment plant. The rainwater pond was not large enough to hold all rainwater and so more water came to the waste water treatment plant than could be treated. In 1998 a new big rainwater container was built in order to prevent overburdening of the waste water treatment plant.

The estimated emissions to water from the copper refinery in Pori were in 1997:

Cu	0.50 t/a	specific emission	0.004 kg/t Cu
As	0.14 t/a		0.001 kg/t Cu
Se	0.25 t/a		0.002 kg/t Cu

The total amount of water used was 710,000 m^3/a.

3.2.8 Solid waste management

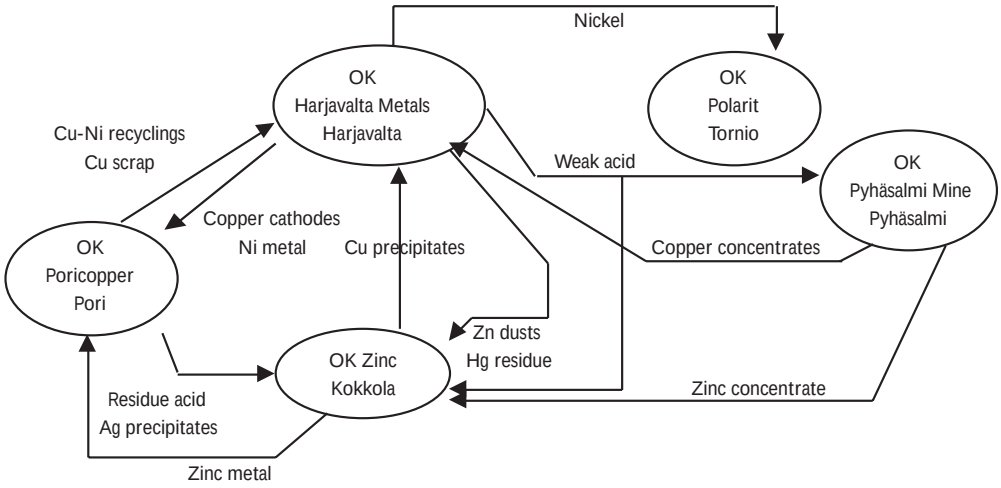

Figure 7. Integration of Outokumpu plants in Finland.

Many of the materials generated during the production of copper can be defined as hazardous wastes. Most of these materials however contain recoverable quantities of copper and other non-ferrous metals and are therefore used as raw materials in their own right. All copper-bearing materials are recycled back to the copper process.

Outokumpu is an integrated metal producer. The integration of the plants is shown in Figure 7. All possible materials are recycled to a plant where they can be used either as raw materials or as chemicals. Harjavalta Metals produces copper

and nickel, Poricopper copper products, Kokkola Zinc zinc and Polarit stainless steel. Pyhäsalmi Mine produces copper, zinc and pyrite concentrates.

In copper smelting, a large tonnage of waste is solid, principally discarded slag. Depending on the copper content of the concentrate, the amount of slag can vary between 0.5 to 2.5 times the quantity of copper produced. The purified slag is fayalite, which consists mainly of iron oxide and silicate. Table 10 shows the composition of typical copper waste.

Table 10. Composition of typical copper smelting waste.

Component	Waste slag from electric furnace %	Final slag from concentrator %
Copper	0.7	0.3–0.5
Iron	37–44	40–44
Silica	27–33	28–30

The final slag is conveyed as sludge to a pond, where the fayalite slag settles to the bottom and the water used is pumped back to the flotation process.

Other solids produced in a copper smelter, such as ladle skulls, scrap, boiler and precipitator dust, are recycled to the smelting furnace and not discarded as wastes. The only solid wastes are the slag and sludges produced in the neutralisation of plant effluents.

All the flue dusts collected in the electrostatic precipitators are fed back to the flash smelting furnace. The dust from the bag filters and the metals precipitated in the waste water treatment plant are also fed to the flash smelting furnace.

The mercury precipitate from the sulphuric acid plant is transported to the company's mercury plant in Kokkola. The weak acid from the sulphuric acid plant is used in Outokumpu's zinc plant in Kokkola and in Pyhäsalmi Mine.

The wastes produced in the copper electrolysis in Pori are transported to Harjavalta and added to the smelting process, if possible. The only waste stored on the plant was the CCA dissolution waste, about 30 t/a.

Finnish legislation demands that dangerous waste must be delivered to organisations which are authorised to handle such materials and take responsibility for their treatment and final destination.Oils and solvents which cannot be recycled and the filters are transported to hazardous waste treatment plant. Unusable metal scrap is sold to the scrap business and paper to a cardboard plant.

3.2.8.1 Overview of the solid wastes produced

Materials to be recycled

slag concentrate	46,000 t/a	to flash smelting furnace
reverts	29,000 t/a	to the converter
Hg-precipitate (acid plant)	50 t/a	to Outokumpu´s zinc plant

Wastes for final disposal

During 1997 the following wastes were formed in Harjavalta:

tailings	350,000 t/a	to the tailing pond
metal scrap	750 t/a	sold for scrap
oils and solvents	150 t/a	to hazardous waste treatment plant
filter materials	75 t/a	to hazardous waste treatment plant
storage batteries and lamps	1 t/a	to hazardous waste treatment plant

3.2.9 Noise abatement

Regarding noise abatement in Harjavalta all possible measures have been taken in order to reduce the noise level from machinery. The noise level in the plant is monitored by the Occupational Health department.

A working group on noise has been established by the City of Pori. This working group commissioned a noise survey of Pori in 1997. Measurements have been done in the vicinity of the Outokumpu site as a separate commission, and the results will be compiled into a noise model comprising the whole of the City of Pori.

3.2.10 Environmental management system

The environmental management system applied in the Outokumpu companies in Pori is in accordance with the EMAS regulation of the European Union.

Internally the environmental management system means that the environmental viewpoint shall be taken into consideration in all fields of operation: in production, maintenance, planning, research etc. The development of environmental management aims at concrete improvements in environmental actions.

The entire staff participates in fulfilling the environmental management system. Each person take the responsibility for the environment. In accordance with the environmental policy, work is performed in a responsible manner, without wasting energy or resources and without harming the environment.

3.2.11 Data management and training

Data management of environmental matters is performed with the use of databases. The system is an active real-time reporting channel and also serves as an environmental manual and archive. All users of the local networks have access to the databases.

The databases improve information distribution, and thus give better opportunities for follow-up and development of environmental procedures.

In order to implement the environmental management system effectively, the whole personnel has been trained to be aware of the effects of their work on the environment, and the possibilities of affecting environmental performance through their own initiative. New workers are familiarised with practical environment work in connection with their on-the-job training.

4 Candidate Best Available Techniques

4.1 General

The pyrometallurgical treatment of copper sulphide concentrates commonly includes two types of operations: smelting and converting. In smelting the concentrate is melted and oxidised with a siliceous or lime flux, which combines with the oxidised iron to form a liquid silicate or calcium ferrite and to produce a solution of molten sulphides. In converting, more sulphur is driven off the sulphide melt, and the remaining iron is oxidised and fluxed for removal as a silicate or calcium ferrite. The final product is blister copper or a matte for further processing.

The pollutants of concern here are the ones associated with liquid and solid wastes and, above all, with gaseous emissions.

Liquid effluents from pyrometallurgical processes are of minor importance because these processes are essentially dry. Liquid effluents come from the cooling water system, from the sulphuric acid plant attached to the smelter and from wet gas cleaning systems. Wet gas cleaning systems, like those required to clean process gases for acid production, remove sulphur trioxide and produce a weak acid. They also collect arsenic, mercury, selenium, and fine dust particles containing other impurities.

In copper smelting, a large tonnage of waste is solid, principally discarded slag. Depending on the copper content of the concentrate, the amount of slag can vary between 0.5 to 2.5 times the quantity of copper produced. Other solids produced in a copper smelter, such as ladle skulls, scrap, boiler and precipitator dust, are recycled to the smelting furnace and not discarded as wastes. The only solid wastes are the slag and sludges produced in the neutralisation of plant effluents.

The major environmental problems in the pyrometallurgy of sulphide concentrates result from the release of SO_2 and particulate emissions which can be categorised as either process or fugitive emissions.

Every smelting process may contain several process units:

- concentrate storage and feed preparation
- drying
- smelting
- slag cleaning
- granulating, drying and grinding
- converting
- anode refining and casting
- gas cooling
- gas cleaning
- acid plant
- tail gas cleaning
- secondary gas cleaning
- waste acid and water treatment

Every one of these process steps must be optimised and must function in the best possible way in order to be BAT. A copper production process is always a compromise, since the process has to produce copper at a saleable and profitable price and

at the same time minimise the use of energy and raw materials and the formation of emissions and wastes.

In this chapter all unit processes are first discussed and compared with each other. Secondly the total processes which consist of unit processes are compared. The comparisons made are based on the literature available.

4.2 Feed Preparation

The concentrates are transferred by conveyor belts up to the dosage silos. Consequently it is unnecessary to store concentrates in open areas and thus emissions decrease. The warehouses have truck washing stations so that spreading of concentrate from the wheels and truck beds can be avoided. These facilities cannot be used in the Northern countries in winter.

Feed preparation is carried out by means of variable speed feeders which unload individual products of known composition from the day storage bins onto a common belt conveyer which takes them to the dryers.

4.3 Drying

4.3.1 Rotary dryer (rotary kiln)

The dryer is fired by natural gas or oil. Nitrogen is sometimes utilised in place of secondary air to control the temperature and also to maintain an oxygen-deficient atmosphere which reduces potential concentrate ignition and combustion. The dry charge, averaging 0.1 % moisture, is discharged through a double trommel screen into a drag conveyor for transport to the pneumatic lift system. Dryer off-gas is directed to an electrostatic precipitator or bag filter for dust removal. All dust is returned to the dryer discharge drag conveyor. Off-gas from the electrostatic precipitator/bag filter passes through an induced draft fan to the stack.

4.3.2 Steam dryer

The multicoil steam dryer has been adapted for concentrate drying on commercial scale in this decade. It consists of a rotor in a stationary receptacle. Heating coils are located parallel to one another. Each set is constructed from several concentric tube rings. The steam from the waste heat boiler system, which is controlled by two reducing stations, serves as a thermal carrier which flows through the coils and is thus used for drying purposes. The steam used is fed back into the steam network and the condensate is recycled back to the feed water system of the waste heat boiler.

The concentrate and additives must be screened before being fed into the coil dryer. For this reason there are screening plants installed in the concentrate conveyeor. The material is screened to less than 15 mm particle size. A magnet separator removes any iron pieces before sieving. The oversize particles are crushed after screening by a crusher and recycled /47/.

The dryer coil spacing has been designed for smooth product flow and less wear and tear. As the exhaust gas volumes are low only a small size bag filter needs to be provided in the dryer to clean off-gases before discharging through a stack to the atmosphere. Dust leakage is very low because the dryer body is stationary and no difficult seals are needed. Additionally the bag filter is integrated to the steam dryer so that the dust drops straight back into the dryer and no other dust

handling or transportation is needed. This results in very low dust emissions. The multicoil dryer is environmentally safe. Only water is evaporated and the gas volume and emissions are minimal. In steam drying the saturated steam produced in the waste heat boiler connected to the FSF can be utilised. This means that part of the chemical energy of the concentrate is used for drying and no extra fossil fuel is needed for heating /48/.

Investment costs for a steam drying installation are low. Operating costs are also low. For example the consumption of electrical energy is only 60 % compared to a rotary dryer. The high efficiency, safety and cleanliness characteristics of this technology have been widely proven /49/.

For the following reasons the steam dryer system has often been chosen instead of the conventional fossil fuel-fired rotary dryer:

a) Low heat losses and a small volume of exhaust gas, resulting in good thermal efficiency in the drying process and low copper losses.
b) No sulphur dioxide emissions and risk of fire outbreak due to the low and even operation temperature of around 120°C.
c) As the volume of gases is low, only a bag filter needs to be provided for dust collection and recycling.
d) Dust leakage is very low as the dryer body is stationary and a good arrangement is possible.
e) The size of the dryer is one third of the conventional fuel-fired dryer. Investment and operation costs are expected to be about 80 % and 50 % of the conventional dryer /44/.
f) The choice of multicoil-type dryers is often based on environmental considerations. The carrier air to absorb the water steam is sucked from the environment in the ratio 1:1. The moist off-gas is dedusted in a jet filter plant. The residual dust content of the off-gas is less than 5 mg/Nm^3 /47/.

The reasons for selecting a multicoil drying plant in preference to a conventional rotary dryer are the relatively simple off-gas system and its sensitivity to material variations (moisture, composition and quantity) and the small space required /47/. The investment and operation costs are low.

4.3.3 Pneumatic drying/Flash dryer

In the flash dryer, the concentrate particles dispersed in the hot gas flow are dehydrated by heat transferred from the hot gas through flow movement. Currently, the flash dryer performs the important role of effective utilisation off-gases from the super heater and the anode furnace.

The pneumatic drying system consists of three parts: rotary kiln, cage mill and pneumatic duct. The feed is scattered, and the moisture is reduced to 3 % or less in the cage mill. At the outlet of the mill, there is a classifying funnel. Coarse material is discharged from this funnel. In the pneumatic duct the moisture is further reduced to 0.3 % or less /45,50/.

Electrical energy consumption per ton of dry concentrate is 10–12 kWh /50/. A comparison of drying systems prepared by Outokumpu Engineering Oy is presented in Table 11.

Table 11. Comparison of drying systems.

Criteria	Spray dryer	Rotary dryer	Steam dryer	Flash dryer	Fluid bed dryer
Investment cost	– –	+ +	+ + +	+	–
Operating cost	– – –	+	+ + +	–	– –
Gas flow	– – –		+ + +	– –	–
Fugitive emission control	–	–	+ + +	–	–
Operational flexibility	–	+ +	+ + +	–	– –
Material handling	+	–	–	–	–
Future expansion	– –	+	+ + +	–	–
Environmental compliance	– –	–	+ + +	–	– –
Process sophistication	+	+	+ +	+	+
Process maturity	+ +	+ + +	+ + +	+ + +	+ +
Generality	+	+ + +	+ +	+ +	+

4.4 Dry Concentrate Conveying System

Dried concentrate should be stored in an intermediate bin and be extracted with a drag conveyer and charged to the dense phase pneumatic conveying system that will convey it to the dry concentrate bin. Air from the pneumatic conveyer will be cleaned in a bag filter and cyclone before venting to the atmosphere through a stack.

4.5 Concentrate Feeding System

The control requirements of a modern high-intensive flash smelting furnace with high oxygen enrichment are at a very high level. The concentrate feeding system must be able to provide a constant and accurate concentrate feed to the burner. High oxygen enrichment means autogeneous operation.

The latest generation of Outokumpu concentrate burner is specifically designed for high oxygen enrichment, wide turn-down ratio and for precise control requirements as well as for high feed rates in both flash smelting furnaces and flash converting furnaces /48/.

4.5.1 Volumetric concentrate feed system

A volumetric concentrate feed system has often been designed for flash furnaces. This system has sometimes been associated with inherent problems such as fluidisation resulting in uncontrolled concentrate exposure to the furnace.

4.5.2 Loss-in-weight feeding system

Outokumpu has developed a gravimetric feed system which is an application of the loss-in-weight feeder. The gravimetric feed system consists of a dosing valve and a dosing bin provided with a screw conveyor underneath.

Both in local and remote mode the operation of the loss-in-weight feeder starts with the filling of the dosing bin. The filling is stopped when the bin is at high level (max) and the feeding is started. When the material reaches the low level the bin is refilled. During refilling the screw conveyer runs at a previously controlled speed until the filling stage is completed.

The material is fed by screw conveyor into a charge drag conveyor which transfers the material further via a concentrate chute into the concentrate burner. This arrangement ensures good accuracy and a constant concentrate feed rate to the furnace.

The loss-in-weight method may even improve the throughput of concentrate compared to a traditional volumetric feeding system with uneven feed. Above all, however, the main benefit of the loss-in weight feeding system is better control of the furnace and also a lower Cu content in the slag /48/.

One important progress step in the development of the process has been the adoption of the loss-in-weight feed system by which the real amount of material entering the furnace can be controlled. This has lowered the time during which the feed mixture and oxygen are not in balance. Thus the clear advantage has been that the amount of magnetite and over-oxidised copper entering the bath has decreased and the average copper content of the slag has decreased /14,31/.

4.6 Smelting Techniques

In the selection of a copper smelting process, the following factors are relevant with regard to their effect on the environment /41/:

- minimum energy requirement by using
  - latent heat of the concentrate
  - oxygen enrichment of combustion air
  - waste heat recovery
- minimum gas volume, causing the lowest emissions, by providing:
  - oxygen enrichment of combustion air
  - as little need as possible for the input of fossil fuels
- low gaseous SO_2 emissions by maximising
  - the SO_2 concentration in smelter gases
  - the proportion of total SO_2 generated in SO_2-rich gas
  - SO_2-conversion efficiency (double catalysis in H_2SO_4 production)
- minimisation of fresh water requirements by
  - internal recirculation and indirect cooling
- minimization of solid waste generation
  - by maximising the recovery of sulphur as sulphuric acid and/or other by products

Table 12 shows the characteristics of various types of smelting furnaces. The continuous Mitsubishi process will be discussed in more detail later in this chapter along with other continuous processes.

The matte grade in flash smelting is nowadays easily raised to 75 %. Mg in the Table is an abbreviation for magnetite. Magnesium has no effects on the flash smelting of copper. The productivity values should not be compared, because they are calculated in different ways for the various furnace types.

In the Outokumpu flash smelting process it is possible to control the matte grade and heat balance independently, which allows smelting irrespective of the composition of the concentrate. Because of the high mass and heat transfer rate in suspension the reactions take place very rapidly and the reaction heat of the concentrate can be totally utilised in the smelting process. This allows the use of oxygen enrichment in order to decrease the gas volume of the smelting process. The ability to withstand high temperatures without destroying the refractory lining is in fact one of the main benefits of the flash smelting process which enables a long campaign life, typically longer than ten years without major rebricking /14/.

Low volume of gas and continuous gas flow from the process facilitates high sulphur recovery. There is no tilting of the furnace and a limited amount of open-

ings through which fugitive emissions could enter the working atmosphere. Because the furnace is operated at a slight underpressure fugitive emissions are minimal. There is no need for a holding furnace which is often a source of fugitive emissions in bath smelting processes. In fact all bath smelting furnaces need a holding furnace or separate settler /14/.

Table 12. Brief specification of various types of smelting furnaces according to Baba and Hondo /42/.

Furnace Type	Productivity T/m² *D	Furnace Charge	Matte grade %	Characteristics
1. Flash Smelting				
Outokumpu	8–11	dry conc.	55–65	environment-friendly process high flexibility for operation high potentiality for expansion high dust generation
Inco	12	dry conc.	45	pure oxygen smelting autogenous operation low dust generation restriction on Mg (low Mg)
2. Bath smelting				
Noranda	15	green conc.	65–75	high flexibility for raw materials (white metal) short brick life of tuyere
Mitsubishi	21	dry conc.	55–70	continuous process short brick life high energy costs due to pressurized air
Teniente	12	green conc.	70–75	high flexibility for raw materials short brick life of tuyere
Oxy-fuel reverb.	5	green conc.	40–45	low Mg and productivity
Vanyukov	80	green conc.	45–70	form smelting high productivity low dust generation
Isasmelt	65	conc.pellet	55	compact furnace using submerged lance low dust generation due to conc.pellet short brick life

The average temperature in the furnace can be maintained at a reasonably low level but the concentrate particle temperature can rise to very high figures for a short period of time before effective heat transfer reduces the temperature of the melted particle. During this period it is possible for some volatile impurities to transfer to the gas phase. This means that impurity elimination in suspension is very effective. In bath smelting processes the impurities dissolve rapidly into liquid phases as the process is slightly closer to the thermodynamic equilibrium. However, in bath smelting processes the gas volume is normally much higher and this also enables impurity elimination into the gas phase in bath smelting processes / 14/.

The bath in the flash smelting furnace settler is relatively quiescent. This enables the separate tapping of matte and slag out of the furnace. It is also a possible to skim slag and tap matte or blister copper out of the furnace continuously. In bath smelting processes, however, the reactions take place in an agitated bath. In these conditions there are better possibilities for the matte particles to coalesce. After a separate settling furnace the copper content of the slag may be closer to the thermodynamic equilibrium. Slag reduction is also easier in an agitated bath. Agitation in bath smelting is made by blowing a high pressure air-oxygen mixture into

the bath or above it. In flash smelting there is no need to use relatively expensive high pressure gas /14/.

There are also some other disadvantages in the flash smelting process compared to bath smelting processes. In the flash smelting process the feed material grain size must be fine enough so that the particles are able to heat up and react in the suspension before hitting the bath in the settler. In bath smelting processes the particle size is not critical at all. The small particle size in flash smelting today is much lower than it used to be some decades ago /14/.

In the flash smelting process the concentrate is dried to a very low moisture content. One could consider this a disadvantage. However, it can be easily demonstrated that drying at low temperatures is most economical because in that case the energy loss is much lower than when water vapour is heated up to actual smelting temperatures /14/.

The Vanyukov furnace has only been used in Soviet areas. It exhibits the highest smelting capability per hearth area among the other types of smelting furnaces, resulting in minimising the cost of constructing the smelter furnace. The furnace is though enough to provide uniform reaction conditions so that lumps of material can be readily processed. Dust generation is low /38/.

In the Mitsubishi furnace the energy costs are high due to the use of pressurised air. The blended feed is charged sequentially to the smelting furnace in batches through charge tanks and conveyed pneumatically through feed pipes to the furnace. The feed pipes are situated in feed lances down which oxygen-enriched air is blown at a velocity of 200 m/s /33/.

IsaSmelt, a compact furnace, has still to solve such problems as splashing and the short brick life of the furnace for its future development /43/.

4.7 Slag Cleaning

4.7.1 Electric furnace

Copper smelting furnace slag is tapped through slag tap holes along launders into the electric furnace. Coke and reverts are added through the furnace roof. Slag from the electric furnace is tapped into granulation and transported to the slag storage area. Matte from the electric furnace is periodically tapped through tapping holes and launders into ladles and transferred by cranes to Peirce-Smith converters for further treatment.

There are three or six electrodes in the electric furnace to supply energy into the furnace. Electric power is needed for the reduction reactions, heat losses and smelting of reverts. The reductive agent is coke. Electric furnace off-gases are first burned in an incinerator, then cooled and routed through a bag filter to the stack.

4.7.2 Slag concentrator

Molten slag is tapped through tapholes and along launders into ladles, where the slag is cooled with water spraying. After cooling the ladles are transported and unloaded into the slag stockpile. The slag is moved by a front-end loader from the stockpile onto a grizzly where oversized lumps are broken by hydraulic hammer. Metallic copper is separated as a grizzly oversize. The grizzly undersize is transported by a belt conveyor to the screening station where lumps, pebbles and fines are separated into separate bins. Grinding consists of autogenous lump mills and pebble mills. Both grinding stages are equipped with hydrocyclones. Flotation is carried out in three main stages. Recovered copper concentrate is thickened and

filtered by a pressure filter. The filtered concentrate is conveyed into the dryer. Slag mill tailings are pumped into a nearby tailing area. The clarified water from the tailing pond is used as process water.

The energy consumption of the slag concentration plant (60–65 kWh/t) is far less than the energy consumption of an electric furnace. The slag concentration plant operates flexibly, adapting to great variations in the feed and even a possible shutdown of the mill does not affect smelter operations. The electric furnace might shut down the whole smelter if disturbances occur. Copper recovery is very high with low copper content in the tailings /51/.

4.8 Converting

The technological innovations in sulphide converting have lagged behind the primary smelting processes. During the past few decades new smelting technologies have been developed, e.g. Outokumpu flash process, INCO flash process, Mitsubishi continuous smelting process, Noranda reactor, dry concentrate injected el Teniente process (CMT), ISASMELT process and CONTOP. All these processes have proven their commercial viability. On the other hand, the Peirce-Smith converter has been the undisputed converting vessel /52/.

The Peirce-Smith converter has served the industry well since its inception. It is, however, fast becoming obsolete because of new developments in technologies and very stringent environmental regulations /52/

Continuous converting is appreciated as superior in performance as it produces a steady stream of high-strength SO_2 gas. It can also meet present and future environmental regulations /52/.

Operation with a very low matte grade close to the natural matte grade is not economical because, in that case, the latent energy of the concentrate is not well utilised in the primary smelting step and excess fuel has to be used to control the heat balance. As a matter of fact it is easier to operate with a high matte grade which is favourable for feeding to the FCF-process which in fact, is the only converting process which can be decoupled for a while from the whole smelting process chain. This allows higher on-line availability for the whole process /14/. The solid matte used also allows high levels of oxygen enrichment /43/.

Operationally, the converting furnace is easy to operate and because the process is continuous, it does not require cranes and ladle transfer. Thus corresponding fugitive emissions into the working space are avoided. In addition to this the launders utilised to convey the matte to granulation can easily be covered to collect and treat the particulates and fumes /14/.

The flash converting process itself has been successfully proven as an effective commercial method of converting matte directly to blister copper /31/.

Table 13 is based on an article by Irshad A. Rana &Co /52/, which was updated by Outokumpu. It indicates that Outokumpu-Kennecott and Mitsubishi continuous converters are the highest-ranked processes primarily because of smaller off-gas handling and acid plant requirements, plus their ability to contain fugitive emissions and meet environmental requirements.

Gas flow in the Outokumpu-Kennecott process is lower, because it is possible to use higher oxygen enrichment (about 80 %) than in the Mitsubishi process (32 %). Outokumpu-Kennecott converting also operates independently of the smelting furnace.

Table 13. Comparison of converting systems /52/.

Criteria	Peirce-Smith converter	Flash converting	Mitsubishi converting	INCO flash converting	ISA/AUS converter
Investment cost	–	+	+	+	– –
Operating cost	–	+	+ +	+	–
Acid plant size	– – –	+ + +	+ +	+ +	+
Operating mode	– –	+ + +	+	+ + +	+
Continuous/batch					
Off-gas characteristics	– – –	+ + +	– –	+	– –
Fugitive emission control	– – –	+ +	+ + +	+	– –
Operational flexibility	+ +	–	– –	–	+
Material handling	– – –	+ +	+ + +	+	+
Slag cleaning	– –	+ +	+	+	–
Future expansion	+	– –	– –	– –	–
Environmental complience	– – –	+ + +	+ + +	+	– –
Impurity removal	+ +	–	+	–	+
Process sophistication	– – –	+ +	+	+	– –
Process maturity	+ + +	+ +	+ +	– –	– – –
Generality	+ + +	–	+	– – –	– – –
Scrap	+ + +	– – –	– –	– – –	+
Producing of reverts	– – –	+ + +	+ + +	+ + +	+ + +

4.9 Anode Furnace

Blister copper is transferred to the anode department or fed into the anode furnace by blister ladles. It is refined by injecting oxygen-enriched air through tuyeres in order to remove sulphur from the copper. Then the dissolved oxygen content is reduced to target levels by injecting a gaseous reductant (e.g. propane or a mixture of steam and natural gas). The refined anode copper is then cast on a wheel utilising double mould casting and automatic weighing.

Furnace gases are sent to an incinerator for complete combustion and can be scrubbed in an alkaline scrubber before venting through the stack. Anode furnaces are covered by a movable hood construction.

4.10 Gas Cooling

Recent copper smelter installations and modernisations include applications of the following technologies: the Outokumpu Flash Smelting Process, the INCO Flash Smelting Process, the Mitsubishi Process, the Noranda Process, the El Teniente Process, the IsaSmelt Process, and the Contop Process. Table 14 provides a representative list of the type of gas handling systems associated with these smelting processes /53/.

Outokumpu Flash Smelting and the Mitsubishi Continuous Smelting Process utilise horizontal waste heat boilers for cooling the off-gas and ESP for particulate removal. Since the Outokumpu process utilises oxygen-enriched air, a large volume of off- gas containing considerable heat exits from furnace. Recovery of this available heat is an important economical factor for this process /53/.

The INCO Flash Smelting Process is based on using bulk oxygen for smelting which results in a very low off-gas volume with little sensible heat content. A proven gas cooling / cleaning technology applied to this process is a close-coupled

saturation tower for gas conditioning followed by a wet scrubbing-based gas cleaning system /53/.

The Noranda Process and El Teniente Process utilise an evaporative spray cooling chamber to condition the furnace gas prior to the hot electrostatic precipitator/53/. The CONTOP Cyclone Process is equipped with a vertical waste heat boiler and uses an ESP for particulate removal /53,40/. The IsaSmelt Process utilises a FLUXFLOW circulating fluid bed waste heat boiler followed by an ESP or a vertical waste heat boiler followed by an ESP /53/.

Table 14. Review of smelting process gas handling systems /53/. ESP = electrostatic precipitator.

Facility	Smelting process	Conc. rate t/day	% O_2 in blast	Furnace off gas			Dust loading	Gas Cooling	Gas Cleaning
				Volume Nm^3*10^6	Temp. °C	SO_2 %	g/Nm^3		
BHP Copper	Outokumpu	3800	50-70	1400	1320	25	1100	Horiz.Boiler	ESP
Kennecott	Outokumpu	3000	70-90	670	-	44,8	-	Horiz.Boiler	ESP
P.D.Hidalgo	Outokumpu	2200	35	1500	1300	22	2600	Horiz.Boiler	ESP
Harjavalta	Outokumpu	1600	75-95	350	1370	25-50	3500	Horiz.Boiler	ESP
Tamano	Outokumpu	1360	35	880	1050	13,5	1200	Horiz.Boiler	ESP
P.D.Chino	Inco	2280	95	280	1200	80	3500	Sat.Tower	Scrubber
Inco	Inco	3200	95	340	1260	70-80	2800	Sat.Tower	Scrubber
KCML	Mitsubishi	1600	40-45	570	1200	25	1100	Horiz.Boiler	ESP
Noranda	Noranda	1600	35-40	2100	820	15	200	Spray Cooler	ESP
Caletones	Teniente	1600	28-30	2200	820	15	200	Spray Cooler	ESP
Cyprus Miami	Isasmelt	2000	50	1300	1120	12	400	Vertic.Boiler	ESP

The gas handling systems mentioned above are the systems used in existing plants. Other gas handling systems can be used as well. Table 15 gives a comparative summary of alternatives including advantages, disadvantages and design considerations. The table was prepared by Paykan Safe and David M. Jones /53/.

There is no waste heat boiler in the INCO-process. Some Vanyukov processes also lack waste heat boilers /14,38/.

In Japan energy costs are very important. The Japanese recover even a small amount of energy through the waste heat boiler /14/.

4.11 Dust Separating

Non-ferrous metal processing plants use both wet and dry dust, mist or fume collectors at various steps in the gas cleaning process. Following the roaster or smelter, a mechanical dust collector, such as a cyclone, is utilised to reduce dust loading to a level of about 230 mg/m^3 /54/.

Electrostatic precipitators are the most common dust or fume collection devices utilised after the hot dust collector to reduce the dust burden even further. The gases are cooled down to the 420–450 °C range prior to the ESP and, in many plants, heat recovery equipment has been found profitable. ESPs are typically sized to remove particulates at 98 to 99 % efficiency so that the off-gas leaves the ESPs with dust loadings of about 20 mg/m^3 to 50 mg/m^3 /54/.

If arsenic removal from the SO_2 laden gas is necessary, a gas cooling tower is utilised to cool the gases to around 115 °C to condense out arsenic fumes. A fabric filter is introduced after this step to remove the arsenic compounds and most of the remaining dust fromthe gas stream /54/.

The cleaned smelter off-gases enter the gas cleaning section prior to the acid plant.

Table 15. Comparison of gas cooling alternatives /53/.

Alternatives	Waste Heat Boiler and ESP	Wet System	Spray Chamber and ESP
Gas Cooling	Waste Heat Boiler	Saturation Tower	Spray Chamber
Gas Cleaning	ESP	Wet Scrubber	ESP
Advantages	steam generation boiler is a good sulphation chamber reduces heat load and gas volume dust segregation low pressure drop	Minimum air infiltration handling cold gas high campaign life good in plant environment reasonable implementation	dust segregation minimum equipment and capital cost low operating costs/ energy requirements easy to implement in retrofit
Disadvantages	potential tube leaks moderate air infiltration layout difficulties difficult in retrofit need air at WHB inlet for sulphation high maintenance due to build-up at convection section	minimum dust segregation high energy acid pipeline corrosion no heat removal water usage/effluent handling fan noise	no heat removal high air infiltration high maintenance poor in-plant environment need for air/O_2 uptake for non-rotary process vessels
Design considerations	fouling of tubes pluggage of interconnecting flues rapid build-up at WHB interface rapping systems expansion between radiation and convection section	need after burning of S/H_2S hot/cold interface build-up acid resistant refractory coarse solid separation venting of weak acid tanks	spray pattern/droplet evaporation controls potential of sticky dust handling

4.12 Sulphur Fixation

Sulphur can be fixed in metallurgical processes by at least one of the following four processes:

- Sulphuric acid production
- Gas scrubbing and gypsum production
- Liquid sulphur dioxide manufacture
- Elemental sulphur production

All of the processes above benefit from high sulphur dioxide concentrations in the gas stream, both economically and in terms of conversion efficiencies. The production of liquid sulphur dioxide and elemental sulphur both require high sulphur dioxide concentrations. Due to the use of oxygen-nriched air in the processes this can easily be achieved.

Sulphuric acid production is the most widely used process for two reasons. Firstly it is the easiest and least expensive sulphur fixation method which does not require high sulphur dioxide concentrations in the off-gas. Secondly the market for sulphuric acid is much larger than for the other products in many locations.

The production of gypsum through the addition of limestone to an ammonium sulphite solution, which is produced from sulphur dioxide, is not as cost effective as sulphuric acid production. It would also require the handling of many

tonnes of limestone, which is required as a reagent in the process, and of the subsequent large amount of gypsum produced.

The production of liquid sulphur dioxide would provide a good return on investment if there were a large market demand. Elemental sulphur production requires a high sulphur dioxide concentration in the off-gas. The feasibility of such a process requires a local market and the availability of a low cost reductant.

The fuel and energy requirements for the fixation of sulphur from low sulphur dioxide concentration streams can be found in Table 16. The primary energy required for any sulphur fixation plant is the energy needed to operate the main blowers that route the gases through the acid plants. The most economical process is the production of sulphuric acid from a continuous gas stream /55/.

Table 16. Fuel and energy requirements for sulphur fixation.

Per tonne of SO_2 fixed	Sulphuric acid produced from			(Gypsum)	
	Continuous gas stream	Variable converter gas stream	Combined continuous & variable	Ammonia dual alkali scrubbing	Elemental sulphur production
Feed gas (SO_2 %)	12	5–8	variable	9–12	9–10
Electric power for main blower and related equipment kWh/tonne	118	219	152	175	350
Coal for reductant kg/tonne	–	–	–	–	330
Natural gas, for start-up Nm^3 /tonne	2,8	3,6	2,5	19,1	22,8
Acid neutralization Electric power for pumps, etc. kWh/tonne	52	52	52	–	–
Total power required kWh/tonne SO_2 fixed	170	271	204	175	350

Although the Sumitomo Toyo smelter utilises the traditional Outokumpu flash smelting process and Peirce-Smith converters, it has distinct differences from other smelters around the world which utilise that same technology. It is one of the cleanest smelters in the world. The sulphur fixation at Toyo is 99.9 %. This is accomplished through a fugitive gas collection system, automated charging of converters and tail gas scrubbing (Table 17). Many facilities have recently installed fugitive gas collection and treatment systems in order to reduce emissions to an acceptable level /14/.

Table 17. Toyo sulphur distribution.

Item	Distribution %
Sulphuric acid	95.8
Gypsum	2.9
Slag	1.1
Water treatment	0.1
Emission	0.1
Total	100

At the Toyo smelter the amount of heavy oil used as fossil fuel in the smelter has been substituted sequentially by less expensive coal /29/.

4.13 Acid Plant

The performance of a metallurgical acid plant is dependent on the performance of the gas cleaning section. If the cleaning system is not effective in removing impurities from the incoming gas, the performance of the contact section will deteriorate. Although the design of wet gas cleaning systems may differ widely, they have the following requirements and features in common:

- Solid contaminants must be removed, giving a final gas quality of 1–2 mg solid/Nm^3
- The sulphur trioxide content of the gas must be reduced to the level of 15–25 mg/Nm^3
- Fluorides and chlorides must be removed to prevent damage to the downstream tower brickwork and converter catalyst
- The gas must be cooled to a temperature of approximately 35-40°C to satisfy the acid plant water balance

Operating at a gas strength of 14 % SO_2 reduces equipment sizes, due to the reduced gas volume. It is estimated that the reduction in capital cost is 25 % and the main compressor horsepower is reduced by 40 %, even compared to a plant designed for 10 % gas. Moreover, pumping power will also be reduced by virtue of the lower circulation rates in the high efficiency drying and final absorber towers /57/.

Table 18. Acid plant size with oxygen enrichment variation (Matte grade at 60 %).

Oxygen enrichment	35 %	49 %	55 %	65 %	70 %
Concentrate smelted t/d	2424	2424	2424	2424	2424
Matte t/d	1486	1486	1486	1486	1486
Oxygen t/d	343	405	420	436	442
FSF process gas					
Volume kNm³/h (wet)	43.7	28.3	24.7	20.4	18.9
SO_2 %	19.6	30.2	34.6	41.7	45.2
FSF process gas to acid plant					
Volume kNm³/h (wet)	78.8	53.5	47.6	40,6	38.0
SO_2 %	10.9	16.0	17.9	21.0	22.4
Peirce-Smith converter process					
Gas (avg.) to acid plant					
Volume kNm³/h (wet)	175.1	175.1	175.1	175,1	175.1
SO_2 %	4.9	4.9	4.9	4.9	4.9
Avg. process gas to acid plant					
Volume kNm³/h (wet)	253.8	228.6	227.7	215.8	213.2
SO_2 %	6.8	7.5	7.7	8,0	8.1
Converter scheduling					
Volume kNm³/h (wet)	366.3	341.0	335.1	328.1	325.5
Acid plant capacity, 10 %					
Design factor, kNm³/h (wet)	400.4	375.1	369.2	362.2	359,6
Relative capital cost factor	104 %	100 %	99 %	97.9 %	97.5 %

With flash smelting technology and a slightly revised contact section, the gas strength and volumetric savings can be pushed even higher. At the Olympic Dam site in Australia (direct blister producing), a preconverter was used to allow operation at 18 % SO_2. In this case, the aim was higher capacity, while maintaining the standard 99.7 % conversion /57/.

One of the opportunities of high gas strength is the excess heat it makes available. In the modern smelter sulphuric acid plant, this heat represents potential income in the form of electrical power /57/.

Sulphur dioxide emissions can be maintained at less than 100 ppm representing 99.95 % collection efficiency of the 14 % SO_2 in the feed gas. Under normal operating conditions SO_2 emissions are in the 30–60 ppm range /31/. Table 18 shows that increasing enrichment is accompanied by a corresponding decrease in the off gas volume from the flash furnace. Since matte grade is in this example held constant at 60 %, the gas volume to the acid plant from the converters does not change /59/.

The Kennecott Garfield smelter is said to be the cleanest smelter in the world. It uses Outokumpu Flash Smelting and the Outokumpu-Kennecott Flash Converting system. Their SO_2 emission rate is 2.6 kg/tonne of copper. To achieve this value they have also a very modern acid plant.

Dyna Wave scrubber systems were selected because of their high collection efficiency and open, robust design. The gas cleaning system consists of two stages of Reverse Jet scrubbing followed by two stages of mist precipitators /57/.

There are some gas booster blowers in order to meet the extremely stringent product quality requirements, especially with regard to heavy metals /57/.

The contact section of the acid plant generally follows the well-proven Monsanto Enviro Chem 3:1 IPA arrangement. Caesium is used as catalyst. With this design and the oxygen-enriched feed gas, conversions of 99.9 % can be reached. This translates to a gas effluent with less than 100 ppm of SO_2 /57/.

The acid plant employs a boiler and superheater to recover sensible heat and a Monsanto Heat Recovery System to recover the absorption heat. The heat recovery towers have proven to be easy and safe to operate /57/.

4.14 Tail and Secondary Gas Cleaning and Scrubbing

Acid plant installations with tail gas scrubbing are becoming common /14/. Secondary emissions are gases and dust from tap holes, transfer pots, etc. It is possible to control these emissions so that they contain sulphur less than 0.1 % of the input of the smelter. It is also necessary to recover dust emissions. To achieve such levels, a myriad of exhaust vents, blowers and auxiliary equipment must be added which further increase the energy consumption. As an example of the requirements needed for such a “clean” operation, an engineering study was made on a 150,000–200,000 tonne/year copper plant. Table 19 gives the energy requirements for such an operation with respect to the smelter area alone /55/.

These fugitive emissions come from feed handling equipment, the dryer, furnaces, matte and slag granulation systems etc. They can be treated with bag filters and scrubbers. One possibility is to use calcium hydroxide $Ca(OH)_2$ which has a high surface area as an absorbing agent. The reaction product is recirculated several times to exploit it as far as possible. The end product is a mixture of dust, calcium sulphate as well as additive residue which is fed to the flash smelting furnace. A cleaned gas dust content of less than 1 mg/Nm^3 can be achieved in the cleaned off- gas from the connected baghouse /47/.

All of the environmental control equipment must be continuously monitored to ensure compliance.

Table 19. Energy requirements for control of fugitive emissions.

Smelter Area	Design Capacity of exhaust fan Nm^3/h	Total Annual energy consumption kWh/year
Concentrate and flux receiving and handling	377 000	1 080 000
Smelting furnace, hood, ladle pits, launder covers, etc.	187 000	750 000
Slag return launder hood	374 000	220 000
Total power required for fugitive emission control for smelter area alone		2 050 000

4.15 Waste Acid and Water Treatment

The weak acid generated in the gas cleaning section typically contains 1–20 % H_2SO_4. Halides will be present as HCl (10–1,000ppm) and HF (10–1,000 ppm including H_2SiF_6). The acid may also contain metals such as copper, zinc and iron (each up to 2,500 ppm), mercury (up to 1,900 ppm) and lead (up to 50 ppm). Arsenic may be present up to levels of 10,000 ppm. Other elements, such as aluminium, nickel, chromium, cadmium, bismuth, antimony, etc. may also be present depending on the contaminants present in the smelter feed. The weak acid will also be saturated with SO_2 (typically between 2,000 and 5,000 ppm depending on the SO_2 strength) /56/.

A typical method for removing arsenic from dilute sulphuric acid is to add a ferric salt and an oxidant to precipitate ferric arsenate at a pH value between 2.5 and 3.0 (< 0.5 % H_2SO_4) /56/.

Most of the selenium will be volatilised during roasting or smelting. Under oxidising conditions, selenium will enter sulphuric acid as selenious acid. However, it is rapidly reduced to elemental selenium. Selenium is recovered from the weak acid by filtering /56/.

Weak acid can be used in hydrometallurgical leaching processes and in flotation processes. The most common treatment for weak acid effluent, which can not be used elsewhere, is lime neutralisation. This produces large amounts of gypsum which is frequently contaminated with potentially toxic metal compounds and therefore must be stored or disposed of. The advantage of this approach is that it is well established and uses relatively straightforward equipment. The acid passes into reaction vessels into which lime slurry is added to form soluble calcium sulphate and insoluble hydroxides of metals such as lead, zinc and copper. Air and a ferric salt may be added to promote the precipitation of ferric arsenate. The presence of ferric ions also assists in the removal of mercury. Fluorides will be precipitated as calcium fluoride but chlorides will remain in solution. The slurry is thickened and the overflow is discharged to the environment. In order to achieve optimum performance of the neutralisation system, it is important to maintain pH control and to monitor and control the ratio of certain components /56/.

The disadvantage of the neutralisation process is that the gypsum which is produced is usually not of a quality high enough to be sold. Therefore the produced gypsum has traditionally been stored /56/.

However, in many locations, storage space is limited and concerns exist that potentially toxic contaminants in the gypsum may leach to the groundwater. Therefore, there is a growing tendency to encapsulate the gypsum in the furnace slag either via external addition of the gypsum to the molten slag or by recycling the gypsum sludge to the smelting furnace /56/.

Many plants have an effluent treatment plant which can treat acidic discharges, process water and contaminated site water. Metals are precipitated with sodium hydroxide or lime. The sludge formed is led to clarification basins. The filtered overflow can be discharged to the waterways. The metal precipitates can be fed to the smelting furnace.

4.16 Comparison of Copper Smelting Processes

Information on copper smelters has been collected in Table 20. The data is from 1995 and has been taken from CRU reports. It is very difficult to compare plants in various countries and geographic locations. For example labour legislation, climatic conditions, in-plant transport costs, energy availability, available infrastructure, special environmental protection requirements etc. influence on operating costs. However, many interesting trends can be seen. The whole smelting process is included in the figures in Table 20 beginning from the drying of the concentrate up to the acid plant.

There are huge differences in the amount of man-hours needed to produce one ton of copper. In one plant one man-hour is needed and in another 285 man-hours. It seems that there are many workers in the plants in the former Soviet Union and very few in Japan. One important thing is today's trend of outsourcing. Does the plant employ all the people working for them or does it buy some of the services needed from outside companies? In the latter case the amount of employees is much smaller.

The total electricity used in the smelter varies from 380 to 867 kWh/tonne of concentrate. The average is about 700 kWh. The Mitsubishi process has the highest consumption. One plant with the combination of reverbatory furnace, El Teniente and Peirce-Smith converters uses only 425 kWh/tonne of concentrate, but its sulphur recovery is only 5 %!

It was mentioned earlier in this chapter that sulphur recovery can be improved by adding tail gas scrubbing procedures. It is interesting to compare the percentage of sulphur recoveries in the plants which use Outokumpu flash smelting, as most plants with double contact acid plants recover 98 % or more. Of the single contact plants one recovers 95 % and the two others 50 and 75 %.

Only some SO_2 emissions are given in Table 20. The Outokumpu-Kennecott flash smelting-flash converting plant emits less than 3.5 kg SO_2/tonne of copper. The Mitsubishi process emissions are about 14 kg SO_2/tonne of copper. Two other plants using Outokumpu flash smelting and Peirce-Smith converting emit 18 and 26 kg SO_2/tonne of copper.

Figure 8 shows the SO_2 emissions in the integrated Harjavalta plant. The upper part of the figure presents the total emissions and the lower part the specific emissions per tonne of metal produced. The permit limit since 1.1.1997 is 4,500 t/a. The big decreases in the amount of SO_2 are all due to having more capacity in the acid plant. The double contact acid plant was built in 1994. After that SO_2 emissions decreased from 5,000 tons to 3,300 tonnes per year. The decrease from 9,000 to 5,200 tonnes per year in 1991 was due to changing the drying method of the concentrate. Earlier the concentrates were dried in a higher temperature, which caused SO_2 emissions. In 1997 the specific emission of SO_2 was only 16 kg/t of metal despite the expansion of the production of copper and nickel /68/.

Table 20. Comparison of copper smelters.

Concepts	New anode t	Capacity t/h	O_2-enrichm. of smelting %	Natural gas m^3/t conc.	Fuel oil kg/t conc.	Matte grade %	O_2-enrichm. of converting %	Oxygen consumption kg/t new Cu*
Steam coil, OK flash smelter (direct blister), electric furnace, double contact	61 000	13	75-95		56			
Rotary dryer, OK flash smelting, electric furnace, Hoboken converter (3), double contact	144 000		65	46		85		
Rotary dryer, OK flash smelting, slag flotation, OK flash converting, Monsanto double contact	268 000	85	65-75	26		75	65-75	1700
OK flash smelting, slag flotation, P-S converter (5),double contact	351 000	115	43	54		65	21	800
Rotary dryer, OK flash smelting, electric furnace, P-S converter, double contact	210 000	97	40-45		44	60	23.5	700
Steam dryer(2), OK flash smelting, slag flotation, P-S converter (3)double contact	104 000	90	95		24	68	26	
Rotary dryer, OK flash smelting, electric furnace, P-S converter (3)Chemico double contact	196000 (210 000*)	80	35		40	58 (67*)	26	
Rotary dryer, OK flash smelting, electric furnace, P- S converter (3),double contact	178 000	80	60-70		40	58	25	
Rotary dryer,OK flash smelting,electric furnace, P-S converter (3), double contact	182 000	80	55			60	24	750
Rotary dryer, OK flash smelting, settling chamber, P-S converter (4), double contact	189 000 (192 000*)	75	27		40	50 (58-60*)	21	
Rotary dryer, OK flash smelting, electric furnace, P-S converter (3), double contact (3)	350 000	70	42		40	60	24	
Rotary dryer (2), OK flash smelting (2), settling chamber, P-S converter (6),double contact (3)	312 000	2*70	32		40	60	21-26	
Rotary dryer, OK flash smelting, electric furnace, P-S converters (3), double contact (3)	230 000	63	38		40	60	23	
Flash dryer, OK flash smelting, settling chamber, P-S converter (3), Monsanto double contact	212 000	72	34		57	61	25	
Rotary dryer, OK flash smelting, electric furnace, P-S converter (2), single contact	54 000	35	32		37	50	25	
Rotary dryer, OK flash smelting, electric furnace, Hoboken converter (3), double contact	165 000	70	60		44	60	24	800
OK flash smelting, slag discard, P-S converter (3) single contact	115 000	55			47	60		850
Rotary dryer (2), OK flash smelting, slag flotation, P-S converter (3), single contact, double contact	28 000	120	50		37	50	25	
Rotary dryer, OK flash smelting, slag flotation, P-S converter	10 000				33	50		
Rotary dryer, OK flash smelting, electric furnace, P-S converter (3), double contact	105 000		36-40		44	52.5		
Rotary dryer, OK flash smelting, slag cleaning furnace, P-S converter (2),single contact	15 000	9			40	50		
Rotary dryer, OK flash smelting, slag flotation, P-S converter (2), single contact	33 000	36			42	47		
Rotary dryer, OK flash smelting, slag flotation, P-S converter (2), single contact	32 000*				93	50		
Fluid bed dryer (2), Inco flash (2), slag discard, MK furnace, Monsanto double contact	114 000	2*83	100	28		49		
Fluid bed dryer, Inco flash, settling furnace, P-S converter (5), double contact	160 000	63	95	29		60	21	900
Fluid bed dryer (2), Inco flash, discard slag, P-S converter (4), double contact	157 000	80	90	23		50	23	1100
Rotary dryer, Mitsubishi continuous, electric furnace, Mitsubishi continuous, double contact	122 000	70	48-50 (40-45)	61		67 (68-69)	32 (30-35)	900
Rotary dryer, Mitsubishi continuous, electric furnace, Mitsubishi continuous, single contact (2)	202 000	120	43		35	69	28	
No dryer, Noranda reactor, slag flotation, P-S converter (4), double contact	220 000	100	35-40	51		71	21	1000
Fluid bed dryer, reverberatory, El Teniente converter (2), P-S converter (4), single contact	180 000	40	30		35	47	30	730
Rotary dryer (3), OK flash smelting, slag flotation, El Teniente (2), P-S converter (5), single contact, double contact	442 000				47	50		900
Rotary dryer, Isasmelt,electric furnace, Hoboken converter, double contact	147 000		50*	57		52 (58-60*)	21	800
Hyperbaric filters, reverberatory, Isa smelt, P-S converter (3)	136 000				67	60		
Fluid bed dryer, Contop, settling furnace, P-S converter (3), double contact	100 000			43		70	21	1150
Rotary dryer (2), Vanyakov (2), settling, P-S converter (8)	300 000		25-35		23	55	21	

Table 20. Comparison of the smelters (continued).

Concepts	Man-h/ t new anode	Electricity use smelting kWh/ t conc	Electricity use acid pl kWh/ t conc	Electricity use oxygen kWh/ t conc	Electricity use total in smelter kWh/ t conc	Acid plant feed gas SO_2 %*	SO_2 emissions kg SO_2 / t Cu	Sulphur Capture %	Operating cost 1995 $ c/lb Cu
Steam coil, OK flash smelter (direct blister), electric furnace, double contact	3.2	50	95	350	495			97	6.3
Rotary dryer, OK flash smelting, electric furnace, Hoboken converter (3), double contact	9.2	110	170	450	730			95.5	15.2
Rotary dryer, OK flash smelting, slag flotation, OK flash converting, Monsanto double contact	4.8	60	110	450	620	34	~3.5	99	8.8
OK flash smelting, slag flotation, P-S converter (5),double contact	2.3	220	99	284	603	8-10	~26	98	11
Rotary dryer, OK flash smelting, electric furnace, P-S converter, double contact	5	140	135	450	725	8		98	12.6
Steam dryer(2), OK flash smelting, slag flotation, P-S converter (3)double contact	4.5	61	99	220	380		~18	98.1	13.7
Rotary dryer, OK flash smelting, electric furnace, P-S converter (3)Chemico double contact	1.8	150	163	450	763	(13*)		98.4 (99.9*)	21.9
Rotary dryer, OK flash smelting, electric furnace, P- S converter (3),double contact	3.6	50	144	450	644			98	7.7
Rotary dryer,OK flash smelting,electric furnace, P-S converter (3), double contact	8.8	200	101	370	671	10		90	5.3
Rotary dryer, OK flash smelting, settling chamber, P-S converter (4), double contact	3.1	145	193	450	788			96	8.7
Rotary dryer, OK flash smelting, electric furnace, P-S converter (3), double contact (3)	1	130	163	400	693			99.5	19.7
Rotary dryer (2), OK flash smelting (2), settling chamber, P-S converter (6),double contact (3)	1.2	144	163	450	757			99.3	22.9
Rotary dryer, OK flash smelting, electric furnace, P-S converters (3), double contact (3)	4.7	130	163	450	743			97.5	12.5
Flash dryer, OK flash smelting, settling chamber, P-S converter (3), Monsanto double contact	1.5	142	163	450	755			98	23.9
Rotary dryer, OK flash smelting, electric furnace, P-S converter (2), single contact	2.7	120	160	450	730			99	27.5
Rotary dryer, OK flash smelting, electric furnace, Hoboken converter (3), double contact	6.1	140	140	450	730	10		92	9.6
OK flash smelting, slag discard, P-S converter (3) single contact	7	100	150	450	700	8		93	15.1
Rotary dryer (2), OK flash smelting, slag flotation, P-S converter (3), single contact, double contact	55.7	95	100	400	595			90	10.4
Rotary dryer, OK flash smelting, slag flotation, P-S converter	285	70	140	450	660			90	81.6
Rotary dryer, OK flash smelting, electric furnace, P-S converter (3), double contact	6.3	70	120					98	
Rotary dryer, OK flash smelting, slag cleaning furnace, P-S converter (2),single contact	56	140	111	450	701			75	34.7
Rotary dryer, OK flash smelting, slag flotation, P-S converter (2), single contact	37.8	140	197	450	787			50	31.2
Rotary dryer, OK flash smelting, slag flotation, P-S converter (2), single contact	38.6	90	120					95	
Fluid bed dryer (2), Inco flash (2), slag discard, MK furnace, Monsanto double contact	4.4	130	130	450	710			98	15.6
Fluid bed dryer, Inco flash, settling furnace, P-S converter (5), double contact	4.7	155	120	450	725	8-10		97	13.1
Fluid bed dryer (2), Inco flash, discard slag, P-S converter (4), double contact	4.6	130	135	450	715	8-10		95	11.4
Rotary dryer, Mitsubishi continuous, electric furnace, Mitsubishi continuous, double contact	3	227	240	400	867	13	~14	99	9.7
Rotary dryer, Mitsubishi continuous, electric furnace, Mitsubishi continuous, single contact (2)	2.9	144	193	450	787	10.5**		99	24.6
No dryer, Noranda reactor, slag flotation, P-S converter (4), double contact	7.2	150	107	450	707	7-10		75	12
Rotary dryer, reverberatory, El Teniente converter (2), P-S converter (4), single contact	6.5	80	95	250	425	4.2		5	7.3
Rotary dryer (3), OK flash smelting, slag flotation, El Teniente (2), P-S converter (5), single-, double contact	4.9	100	140	450	690	10.2		68	8
Rotary dryer, Isasmelt,electric furnace, Hoboken converter, double contact	3.8	123	164	461	748	8.3 (7.5*)		98.4	9.9
Hyperbaric filters, reverberatory, Isa smelt, P-S converter (3)	3.6	95		350				0	9
Fluid bed dryer, Contop, settling furnace, P-S converter (3), double contact	4.7	100	150	450	700	4-8		96	15.3
Rotary dryer (2), Vanyakov (2), settling, P-S converter (8)	15.8	100	200	400	700			80	

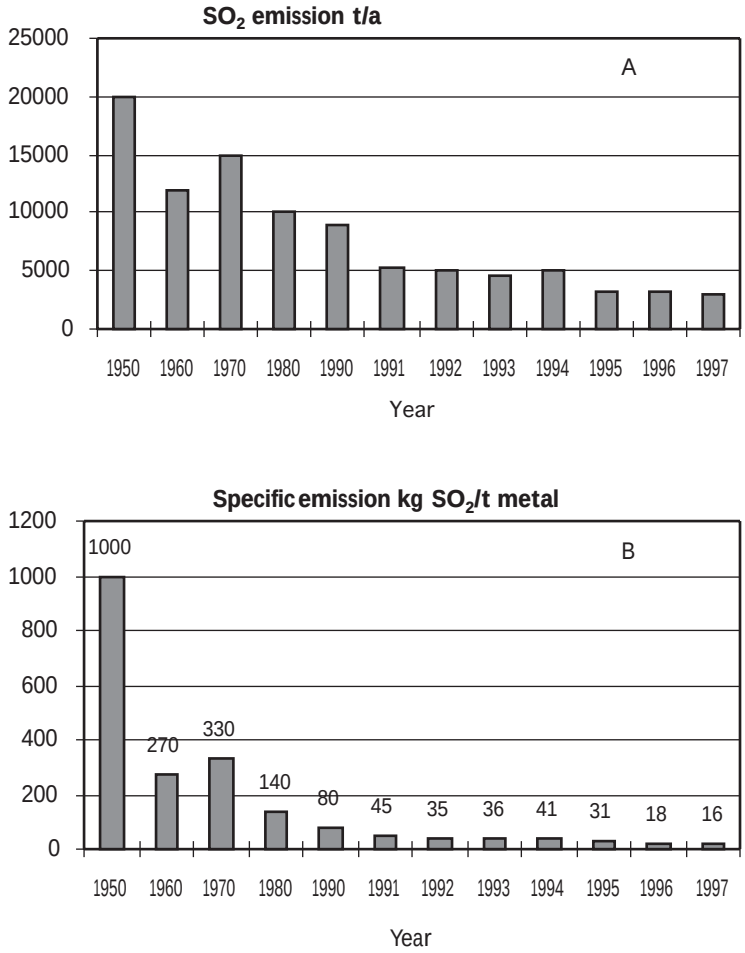

Figure 8. Sulphur dioxide emissions in Harjavalta in the years 1950–1997. A. Total emissions. B. Specific emissions /68/.

The operating costs also vary quite a lot, from 5.3 to 81.6 Usc/lb Cu. The highest figure of course belongs to the plant with many more workers than the others. In the Outokumpu -Kennecott flash smelting-flash converting plant the costs are 8.8 USc/lb Cu, in the plants using the Mitsubishi process from 9.7 to 24.6 USc/lb Cu and in the Isasmelt plants 9 and 9.9 USc/lb Cu.

H.Sohn has compared copper smelting processes and writes /43/:

- The Kennecott-Outokumpu Flash Converting process: The solidification of matte from the smelting furnace has proven to be an effective approach to maximising the inherent flexibility of the smelter by avoiding the problems of maintaining and regulating continuous metal flows. The solid matte allows high levels of oxygen enrichment, and with the well-proven furnace design Outokumpu the process can be designed for a wide range of smelter capacities. Environmental control is exceptional with emissions less than 3.5 kg (SO_2)/ tonne of copper or 99.9+ sulphur recovery, the lowest emission rate in the world.
- The Mitsubishi process is suitable for copper production of up to 200,000 tonnes per year of new metal.
- Bath smelting processes including the Noranda process and the closely allied Caletones Matte Treatment (CMT) process have not yet been demonstrated to meet the highest levels of emission control.

- The Vanyukov foam-bath smelting process for both copper and nickel has been applied at Norilsk, Balkash, and Sredneuralsk smelters, but it has not been adopted outside the CIS countries.
- The IsaSmelt Process and the closely related Ausmelt (also Sirosmelt) process appear to be a good option for smaller plants, particularly ones with a source of secondary feed which can easily be smelted in the reactor.
- The Contop, which stands for CONtinuous smelting and TOP blowing, process has resulted in 98 % sulphur recovery. The process will be closed down in 1999.

The Mitsubishi process employs bath smelting as a continuous process with high reaction uniformity. This process allows a compact facility with high productivity. The disadvantage is that the brick of the furnace ceiling is likely to be substantially damaged owing to the calcium ferrite slag employed in this process and splash erosion resulting from bath smelting. Therefore, it is difficult to keep a high quality working environment. Additionally, the emission load to the periphery of the smelter is relatively high. The brick of the furnace body as a reaction vessel is also susceptible to fusion loss. A large amount of water cooling blocks are used to overcome this problem, resulting in large energy losses. The furnace further requires a large amount of energy to capture fugitive gases, which is also a disadvantage.

4.17 Electrolytic Refining

In the electrolytic refining of copper it is possible to use permanent cathode techniques instead of copper starter sheets. The ISA process uses stainless steel plates, from which the copper cathodes are stripped with automatic stripping machines. Another modern electrolytic refining concept is the Falconbridge/Kidd Creek permanent cathode approach. This technique is very similar to the ISA process. The main difference is the fact that Kidd Creek does not use side and bottom wax and therefore the copper deposits on both sides of the cathode plate grow together at the bottom /2/.

5 Best Available Technique

In the last chapter the various process steps in pyrometallurgical copper production were discussed. It is easy to conclude that there is no unambiguous best available technique. The best available technique consists of optimised unit processes. These unit processes must be designed in such a way that they fit together. All particulate and gaseous emissions must be kept in strict control.

The best available technique consists of the following unit processes:

- The concentrates are stored in warehouses.
- The concentrates are dried in multicoil steam dryers.
- A loss-in weight feeding system is used to feed the concentrate into the flash smelting furnace.
- The concentrate is smelted in the flash smelting furnace using a high oxygen enrichment of air (65–75 %). The gas produced in the reactions in the reaction shaft is cooled and cleaned in a waste heat boiler and electrostatic precipitator before passing through gas scrubbers to the acid plant. All dust collected in the electrostatic precipitators is recycled to the flash smelting furnace.
- The high grade matte is granulated directly from the flash smelting furnace without any ladle transport. The slag is cooled, crushed and ground before flotation for copper recovery. The slag concentrate is fed into the flash smelting furnace together with the primary concentrate. The other option is to use an electric furnace for slag cleaning.
- Copper matte is smelted in the flash converting furnace using high oxygen enrichment. The gas produced in the reactions in the reaction shaft is cooled and cleaned in a waste heat boiler and electrostatic precipitator before passing through gas scrubbers to the acid plant. All dust collected in the electrostatic precipitators is recycled to the flash smelting furnace or the flash converting furnace.
- The molten blister copper is tapped from the flash converting furnace via launders directly into the anode furnace.
- Blister copper is refined in the anode furnace and cast into anodes.
- Copper anodes are electrorefined to copper cathodes by the permanent cathode technique.
- The cleaned gas stream from the furnaces is routed to a modern double contact acid plant for the production of sulphuric acid.
- The plant is equipped with good environmental control equipment:
  1. All feed handling equipment is vented through high-efficiency bag filters.
  2. Dryer gas, after cleaning in a bag filter, passes through a desulphurisation gas scrubber, before being discharged to the atmosphere through the stack.
  3. Secondary gas, primarily from the furnace launder ventilation systems, is exhausted through a four-compartment bag filter, scrubbed using sodium hydroxide and discharged through the stack.
  4. Anode furnace combustion and refining gases are processed through desulphurisation scrubbers which, in addition to controlling SO_2 emissions during the furnace oxidation process, also remove the fine partic-

ulates from the furnace gas. The cleaned gas is discharged to the atmosphere through the stack.

5. The exhaust gases from the matte and slag granulation systems are processed through the secondary gas handling system.

Kennecott Corporation's Magna smelter in the United States uses this Kennecott-Outokumpu Flash Smelting Flash Converting process just as it is described in this chapter. The plant has been designed to treat 1,000,000 tonnes of concentrates a year. Its SO_2 emission levels have been under 3.5 kg SO_2 per tonne of copper, the lowest emission rate in copper smelting plants in the whole world. With current emission and copper production rates, the emission rate is 2.6 kg SO_2 per tonne of copper.

Permit level for particulate matter PM10 is 400 tonnes/year. The actual last 12 months PM emissions have been 276 tonnes.

The Flash Smelting Flash Converting process has the following advantages:

- Low investment and operation costs for the whole smelter including smelting, converting and acid production
- High process energy efficiency
- High on-line availability
- Flexibility to treat a wide range of raw materials
- High sulphur fixation from continuous high SO_2 gas flow, e.g. minimum emissions to the environment and working atmosphere
- Elimination of unnecessary molten material transportation, e.g. minimum emissions of fumes and SO_2 to the environment and working atmosphere
- Low revert formation rate
- Low metal content in vitrified silicate slag
- High degree of automation.

6 Emerging Techniques

It is quite difficult to determine the difference between available and emerging techniques. In this study "available" means that an operating company, following issue of a commercial invitation to tender to a metallurgical engineering design contractor for the construction of a full scale plant, could expect to receive an offer capable of acceptance, including technical and commercial performance guarantees. If such an offer was unlikely to be forthcoming the process/plant should be considered as "emerging". Emerging techniques have, however, been tested on pilot scale and the results and process calculations seem promising.

6.1 Pyrometallurgical Processes

Intensive process development is going on in the copper smelting processes. One emerging flash smelting process is the Kivset process, which is in use in Kazakstan. The Noranda-Mitsubishi continuous smelter will start in 1999. In this process the plant has been retrofitted by combining the Noranda reactor with a continuous Mitsubishi type converting furnace. It makes possible a practically continuous operation from concentrate to blister smelting. The operation of the smelter and the emission values obtainable will be seen in the future.

Researchers already have some vision of the copper smelter of tomorrow. It goes further than today's concept of flash smelting-flash converting. The smelter will have only one single furnace which produces directly blister copper, discard slag and has only one continuous off-gas stream. It could be as follows:

- The flash smelting furnace has two reaction shafts, one for smelting concentrates to matte and one for smelting matte and high grade concentrates to blister. Due to SO_2 recirculation it is possible to use pure oxygen in smelting.
- The slag from the blister copper smelting part runs into a smelting settler and is reduced. The blister is tapped out continuously and is possibly refined before the anode furnace.
- The matte from the primary smelting part is continuously tapped and granulated. The copper content of the slag is reduced in the slag cleaning unit located at the other end of the furnace so that the continuously skimmed slag can be discarded.
- The low dust-containing process gas passes through a gas cooling unit and through dust separation to a new generation acid plant, which is able to produce sulphuric acid without dilution of the high strength process gas. Separated dust is treated so that impurities are bled off in concentrated saleable or inert form. Residue from the treatment unit is then circulated back into the primary smelting unit.

6.2 Hydrometallurgical Processes

Of the many processes that have been proposed for the hydrometallurgical production of copper, the majority have been developed only as far as bench scale.

The driving force behind hydrometallurgical processes is environmental protection, when no SO_2 is produced from sulphide concentrates, but sulphides are oxidised to water soluble sulphates or preferably to elemental sulphur, which is inert and can be stored safely /26/.

Most sulphidic concentrates also contain iron. The problems of iron disposal can be illustrated by the zinc industry, where jarosite, goethite and haematite processes have been used for a long time. The key requirements for a hydrometallurgical sulphide concentrate process are not dictated by the quality of copper, which is easy to achieve with SX-EW, but rather the fates of the major by-products, sulphur and iron. These problems have not yet been solved well enough.

The leaching processes developed far enough that they can be presumed to be emerging techniques, are the Intec process and Cominco´s CESL process. The development of the bioleaching of chalcopyritic copper concentrates is also proceeding fast, as Billiton is developing a “Biocop”-process.

7 Conclusions and Recommendations

About 90 % of the world's copper production from ores is now manufactured from sulphidic ores by pyrometallurgical techniques. Hydrometallurgical copper production has, however, become more important during the last decade. In the year 2000 more than 20 % of copper is expected to be produced by the leaching of copper ores or concentrates.

Only the pyrometallurgical copper process is used in Finland to recover copper from copper concentrates. Selenium, tellurium, silver, gold, platinum and palladium are recovered in the process as by-products.

The pyrometallurgical treatment of copper sulphide concentrates commonly includes two types of operations, smelting and converting. In the smelting phase, part of the sulphur and iron in the concentrate feed is oxidised with oxygen-enriched air at about 1,200°C and a molten sulphide phase (matte) rich in copper is produced. Copper converting consists of air oxidation of the molten matte from smelting. Converting removes the iron and sulphur from the matte and produces crude molten metallic blister copper. The slag formed is discarded after a purification step. Blister copper is fire-refined and cast into anodes. The anodes are electrorefined to pure copper cathodes. The remaining anode slime is further treated to recover the remaining metals.

The main solid waste from the process is the remaining slag which has to be stored in a tailings area. Liquid effluents from pyrometallurgical processes are of minor importance because these processes are essentially dry. Liquid effluents result from the cooling water system, from the sulphuric acid plant attached to the smelter and from wet gas cleaning systems. Wet gas cleaning systems produce a weak acid. They also collect arsenic, mercury, selenium and fine dust particles containing other impurities. The major environmental problem results from the release of SO_2 and particulate emissions.

The best available technique to produce copper from sulphidic concentrates consists of the following unit processes:

- The concentrates are stored indoors and dried in multicoil steam dryers.
- A loss-in-weight feeding system is used to feed the concentrate.
- The flash smelting flash converting process is used.
- The slag is cleaned.
- Blister copper is refined in the anode furnace and cast into anodes.
- Copper anodes are electrorefined to cathodes using permanent cathodes.
- The cleaned gas stream from the furnaces is routed to a modern double contact acid plant.
- The plant is equipped with a good environmental control system.

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Documentation page

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Author(s)	Marja Riekkola-Vanhanen	
Title of publication	Finnish expert report on best available techniques in copper production and by-production of precious metals	
Parts of publication/ other project publications		
Abstract	The main objective of this BAT report is to identify available techniques for the reduction of emissions and energy use in the primary copper production in Finland. Copper is recovered from sulphide concentrates with the pyrometallurgical flash smelting process. The smelting takes place without any external fuel addition, i.e. the chemical energy of the concentrate is utilised for smelting. First, part of the sulphur and iron in the feed are oxidised to form copper matte and slag. Matte is further oxidised in converters to blister copper. The slag formed is discarded after a purification step. Blister copper is fire-refined and cast into anodes. The anodes are electrorefined to pure copper cathodes. The remaining anode slime is further treated to recover the remaining metals. The main solid waste from the process is the purified slag, which is stored in a tailings area. Liquid effluents result from the cooling water system, from the sulphuric acid plant attached to the smelter and from wet gas cleaning systems. The major environmental problem results from the release of SO_2 and particulate emissions.	
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Julkaisija	Suomen ympäristökeskus	Julkaisuaika Kesäkuu 1999
Tekijä(t)	Marja Riekkola-Vanhanen	
Julkaisun nimi	Suomalainen asiantuntijaraportti parhaimmista käytettävissä olevista tekniikoista kuparin ja sen sivutuotteina syntyvien jalometallien tuotannossa	
Julkaisun osat/ muut saman projektin tuottamat julkaisut		
Tiivistelmä	Tässä BAT raportissa esitellään menetelmät, joita käyttämällä voidaan vähentää päästöjä ja energian kulutusta primäärisessä kuparin tuotannossa Suomessa. Kuparia valmistetaan sulfidisista rikasteista käyttämällä pyrometallurgista liekkisulatusprosessia. Se ei tarvitse ulkoista energiaa, vaan tuottaa itse energiansa polttamalla rikkiä ja rautaa. Ensimmäisessä vaiheessa osa syötteen rikistä ja raudasta hapetetaan, jolloin saadaan kuparikiveä ja kuonaa. Kivi hapetetaan edelleen konverttereissa blister-kupariksi. Puhdistettu kuona jää jätteeksi. Blister-kupari puhdistetaan raffinoimalla ja valetaan anodeiksi. Anodeista tehdään puhdasta katodikuparia elektrolyysin avulla. Jäljelle jääneestä anodiliejusta erotetaan siihen jääneet metallit. Prosessissa syntyvät kiinteät jätteet ovat lähinnä kuonahiekkaa, joka varastoidaan läjitysalueelle. Liuenneet epäpuhtaudet tulevat jäähdytysvesisysteemistä, sulattoon liitetyltä rikkihappotehtaalta ja kaasunpesulaitteistoista. Rikkidioksidi- ja hiukkaspäästöt ovat pahin kuparinvalmistuksen ympäristöön kohdistuva haitta.	
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Sammandrag	Målet med den här BAT raporten är att identifiera tillgänglig teknik för reduktion av emission och energianvändning i primär koppar produktion i Finland. Koppar raffineras från sulfidiska koncentrat med flamsmältningsprocessen. Smältningen av koncentratet genomförs utan tillförsel av extern energi eftersom koncentratets kemiska energi kan användas till godo vid smältningen. Först oxideras en del av svavlet och järnet i ingångsmaterialet så att det uppstår en kopparslig och en slagg. Sligen oxideras vidare i konvertrar för att forma blisterkoppar. Slaggen avsätts efter en reningsraffination. Blisterkoppar eldraffineras och gjuts till anoder. Anoderna elektroraffineras till rena kopparkatoder. Det kvar varande anodslammet behandlas vidare för att ta till vara på övriga metaller. De huvudsakliga fasta biprodukterna från processen är slaggen som lagras på området. Avloppsvatten uppstår från processens kylsystem, från svavelsyre-enheten och från det våta gas reningsverket. För de stora miljöutmaningarna står svaveldioxid och partickel emissionerna.	
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